

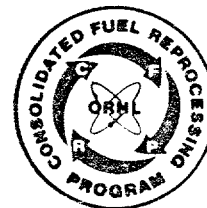


**OAK RIDGE  
NATIONAL  
LABORATORY**

**MARTIN MARIETTA**

**Airborne Waste Management Technology  
Applicable for Use in Reprocessing  
Plants for Control of Iodine and  
Other Off-Gas Constituents**

R. T. Jubin



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**AIRBORNE WASTE MANAGEMENT TECHNOLOGY APPLICABLE  
FOR USE IN REPROCESSING PLANTS FOR CONTROL OF  
IODINE AND OTHER OFF-GAS CONSTITUENTS**

R. T. Jubin  
Fuel Recycle Division

**Date Published: February 1988**

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## ABSTRACT

Extensive work in the area of iodine removal from reprocessing plant off-gas streams using various types of solid sorbent materials has been conducted worldwide over the past two decades. This work has focused on the use of carbon filters, primarily for power plant applications. More recently, the use of silver-containing sorbents has been the subject of considerable research. The most recent work in the United States has addressed the use of silver-exchanged faujasites and mordenites.

The chemical reactions of iodine with silver on the sorbent are not well defined, but it is generally believed that chemisorbed iodides and iodates are formed. The process for iodine recovery generally involves passage of the iodine-laden gas stream through a packed bed of the adsorbent material preheated to a temperature of about 150°C. Most iodine removal system designs utilizing silver-containing solid sorbents assume only a 30 to 50% silver utilization. Based on laboratory tests, potentially 60 to 70% of the silver contained in the sorbents can be reacted with iodine. To overcome the high cost of silver associated with these materials, various approaches have been explored. Among these are the regeneration of the silver-containing sorbent by stripping the iodine and trapping the released iodine on a less expensive sorbent for disposal or, alternatively, initially trapping the iodine on a sorbent that has undergone only partial silver exchange and is capable of attaining a much higher silver utilization.

Once the iodine is captured on the silver, the iodine-containing material must be converted into a form suitable for long-term disposal. A number of fixation forms have been examined for their leach resistance and chemical stability. Some that have been considered are silver iodide fixed in cement and various iodates fixed in cement (such as barium, calcium, strontium, or mercuric iodates). In addition, iodine sodalite appears to be another promising waste form. The selection of the "best" waste form must, of course, be coupled with the disposal strategy or disposal site and the capture-technique employed.

This summary report describes the U.S. work in regeneration of iodine-loaded solid sorbent material. In addition, the report discusses the broader subject of plant off-gas treatment including system design. The off-gas technologies to recover  $\text{NO}_x$  and to recover and dispose of Kr,  $^{14}\text{C}$ , and I are described as to their impacts on the design of an integrated off-gas system. The effect of ventilation philosophy for the reprocessing plant is discussed as an integral part of the overall treatment philosophy of the plant off-gas.

## 1. INTRODUCTION

Iodine-129 is produced by both natural and man-made sources. Of all the iodine isotopes produced, only  $^{129}\text{I}$  has a half-life long enough to pose a potential long-term radionuclide hazard. The natural sources include the spontaneous fission of uranium and the interaction of cosmic rays with xenon in the atmosphere. The annual worldwide production through these natural paths is about 10 mg/year. With its half-life of  $1.7 \times 10^7$  years,  $^{129}\text{I}$  tends to accumulate worldwide. As of 1940, the estimated accumulation was reported to be  $2 \times 10^5$  g (Pence and Staples, 1974). A single light-water reactor (LWR) will produce 234 g of  $^{129}\text{I}$  based on a uranium burnup of 30,000 MWd/t (Burger, 1977). In handling the spent fuel, a single 5-t/d nuclear fuel reprocessing plant would have to process  $3.2 \times 10^5$  g of  $^{129}\text{I}$  per year.

In addition to the  $^{129}\text{I}$ , various amounts of other short half-life iodine isotopes are also produced. However, none of these appear in significant amounts after long (>200-d) decay times. On the other hand, should reducing the decay time to as little as 90 d have economic incentive, larger amounts of the short half-life isotope  $^{131}\text{I}$  ( $t_{1/2} = 8.05$  d; specific activity,  $1.24 \times 10^5$  Ci/g) would also become a significant factor.

The principal release form of iodine during the fuel dissolution step is elemental iodine ( $\text{I}_2$ ); however, organic iodides are produced by reactions with organic contaminants in the dissolver off-gas (DOG) and vessel off-gas (VOG) systems. The predominant compound formed by these restrictions is methyl iodide ( $\text{CH}_3\text{I}$ ), which may amount to several percent of the total iodine in the DOG and VOG systems.





## 2. BACKGROUND

The problem of radioiodine control began with the world's first reprocessing plant at Hanford. Shortly after the plant started operation in 1945,  $^{131}\text{I}$  was found on vegetation near the plant site (Rodger and Reese, 1969). To control the levels of  $^{131}\text{I}$  released, the cooling time of the fuel was increased to allow a portion of the  $^{131}\text{I}$  to decay. A "silver reactor" was then developed and installed to remove the iodine from the DOG system by direct reaction with silver nitrate. Since that time, every large reprocessing plant, except the Nuclear Fuel Services (NFS) West Valley plant, has been equipped with one or more iodine-trapping systems.



### 3. IODINE REMOVAL REQUIREMENTS

The release limits presented in this section are based on historical information; consequently, the design engineer must use the most recent regulations available for his/her country to determine the appropriate limits for the facility of interest.

One of the basic tenets of radioprotection as formulated by the International Commission of Radiological Protection (ICRP) is that, in addition to complying with the relevant national, state and local release limits, "all exposures shall be kept to as low as reasonable achievable, economic and social factors being taken into account" [International Atomic Energy Agency (IAEA), to be published (a)]. This is referred to as the ALARA principle. Moreover, "all proposed installations and new operations (and) all changes in existing installations and operations . . . should be examined at the design stage from the point of view of restricting the resulting operational and general exposure" [IAEA, to be published (a)].

The ICRP has recommended a limit of 0.5 mrem/year to the whole body for members of critical groups, which are defined as groups not subject to occupational exposure expected to receive the highest dose. Where, because of the metabolic properties of the radioactive species involved, the exposure is primarily to one or more organs of the body, different limits are recommended.

Fuel reprocessing facilities are required to have off-gas systems designed "to confine hazardous chemical or radioactive materials evolved during process operations and radioactive waste storage, and to reduce their concentrations in gaseous process effluents to levels as low as practicable" [U.S. Atomic Energy Commission (AEC), 1974]. In addition, all parts of the off-gas system should be designed to meet the release limits for radioactive materials during normal operation. The U.S. Nuclear Regulatory Commission (NRC) has published concentration limits for  $^{129}\text{I}$  and  $^{131}\text{I}$  in the environment. These limits are set forth for the United States in regulation 10 CFR Pt. 20 (National Archives of the United States, 1983). This regulation leaves some leeway on the permissible concentration of radioactive material discharged from the stack, provided that the discharge site is within a restricted area. In the case of a restricted area, the amount discharged may be calculated from the limit set forth in Table II of Appendix B of 10 CFR Pt. 20 by applying the proper factors for dilution, decay, and dispersion between the point of discharge and the boundary of the restricted area. The values for soluble iodine (which are more restrictive than those for insoluble iodine) are presented in Table 1 for controlled and uncontrolled areas.

The U.S. Department of Energy (DOE) Order 5480.1A, Chap. XI, Attachment XI-1 (1981), contains concentration guidelines for  $^{129}\text{I}$  and  $^{131}\text{I}$  in uncontrolled areas that are identical to those of the NRC given in Table 1. However, the values listed in the DOE order for both  $^{129}\text{I}$  and  $^{131}\text{I}$  in controlled areas are lower than those of the NRC. The

**Table 1. Maximum permissible concentration  
of soluble radioiodine in air**

Units	Controlled area		Uncontrolled area	
	$^{129}\text{I}$		$^{131}\text{I}$	
$\mu\text{Ci/mL}$	$2 \times 10^{-9}$	$9 \times 10^{-9}$	$2 \times 10^{-11}$	$1 \times 10^{-10}$
$\mu\text{mol of}$ iodine per liter	$9 \times 10^{-5}$	$6 \times 10^{-13}$	$9 \times 10^{-7}$	$6 \times 10^{-15}$

Source: National Archives, 1983.

DOE value for  $^{129}\text{I}$  in air of a controlled area is  $8 \times 10^{-10} \mu\text{Ci/mL}$ , and for  $^{131}\text{I}$  the DOE value is  $4 \times 10^{-9} \mu\text{Ci/mL}$ . The DOE values reflect a maximum permissible annual dose of 15 rem, whereas the NRC values are still based upon the older occupational limit of 30 rem for the thyroid.

The U.S. Environmental Protection Agency (EPA) has set limits for the combined exposure of the public to radiation from all phases of the LWR uranium fuel cycle. The limits for the individual member of the public are 75 mrem/year to the thyroid and 25 mrem/year to any other organ or to the total body. The EPA thyroid dose limit is 1/20 of that specified in 10 CFR Pt. 20 and DOE Order 5480.1A. To demonstrate compliance with this EPA requirement, radioiodine-monitoring capabilities would have to be about 1 order of magnitude more sensitive than required by the 1983 NRC requirements.

In addition, the EPA has, in its 40 CFR Pt. 190 (National Archives of the United States, 1977), stated limits for the rate of release of certain radionuclides to the environment from the LWR fuel cycle. The limit for  $^{129}\text{I}$  is 5 mCi/GW(e)year. The  $^{129}\text{I}$  generation rate in pressurized-water reactor (PWR) power reactor fuel is about 1 Ci/GW(e)/year. To meet this EPA limit, the iodine collection system at a fuel reprocessing plant must maintain a long-term decontamination factor (DF) of 200 during actual operation. Such a DF, coupled with subsequent atmospheric dilution, would control the environmental concentrations of  $^{129}\text{I}$  to values well below those corresponding to the 75 mrem/year thyroid dose limit.

Many countries have totally adopted the ICRP recommended limits and the ALARA (as low as reasonably achievable) principle. It should be noted that applying the ALARA principle to individual sites results in site discharge limits that correspond to much lower values of exposure than the limits indicated by ICRP. In a number of countries, appreciably lower limits of general application to a given type of installation have been established.

Examples of limits of general application are given in Table 2. These limits are, in some cases, not directly comparable in that they may refer to exposure explicitly or implicitly. They may also refer to variants of the same type of installation, such as a PWR, according to national preference. However, even where directly comparable, they may

Table 2. Effluent release and dose criteria of general application

Country	Limit	Remarks	Reference
France	5 Ci halogens + aerosols/year 80 Ci noble gases	Statutory limit for LWRs of 3000 MW(h)	J.O. de la Republique de la France p. 5496, 12.9.76
Federal Republic of Germany	30 mrem/year, whole body	Gaseous effluents from NPP statutory	
United Kingdom	5 mrem/year sites <sup>a</sup> 1/30th of ICRP limits	Design target for HS/R 167/81 Operational limit for NPP sites	CEGB report HS/R 167/81, rev. 3/82
United States	5 mrem/year, airborne whole body 15 mrem/year, airborne skin 15 mrem/year, iodine + particulates, any organ 25 mrem/year, whole body 75 mrem/year, thyroid 25 mrem/year, other organs	Design targets for LWRs  Operational limits NPP + FRP	10 CFR Pt 50  40 CFR Pt 190
Federal Republic of Germany	Ci/year 0.05 aerosol 5 aerosol 0.2 <sup>129</sup> I 9 × 10 <sup>6</sup> <sup>85</sup> Kr 3 × 10 <sup>5</sup> <sup>3</sup> H 7 × 10 <sup>3</sup> <sup>14</sup> C	1000-t/year proposed regulation	Bundes Anzeiger, No. 128, p. 7027 15.6.83
United Kingdom	10% of ICRP 1% of ICRP	Target for existing plant FRP Target for design of new plant FRP	
United States	50,000 Ci/GW(e)/year <sup>85</sup> Kr 5 mCi/GW(e)/year <sup>129</sup> I 0.5 mCi/GW(e)/year Transuranics with half-lives over 1 year	Operational, FRP	40 CFR Pt 190
ICRP	0.5 rem/year, whole body	Critical group, nonoccupational exposure	

<sup>a</sup>These are quasiofficial limits and do not have regulatory status.

Source: IAEA, to be published(b).

differ markedly. In effect this points out the general lack of uniformity in the interpretation of what upper bounds result from the application of the ALARA principle. In some cases, this can be explained by more rigid local constraints or local conditions.

What is clear from this discussion is that while there is no generally accepted release standards, the design engineer must be familiar with the applicable local and national regulations governing iodine release. With this information and knowledge about the processes available to recover iodine from the process streams, the plant designer can begin to address the problem of iodine control.

## 4. IODINE CHEMISTRY

### 4.1 IODINE FORMS EXPECTED

Table 3 (from Craig et al., 1970) shows the various fission product iodine isotopes, their specific activities, and the amounts expected from a typical fuel.

Those of most concern to the nuclear fuel reprocessing industry include the following.

1. Iodine-131 ( $t_{1/2} = 8.05$  d) is the most important isotope from the standpoint of safety and also in determining radiation exposure limits to power station crews during normal and accident conditions. This isotope is also noteworthy in the reprocessing of short-cooled fuel because of its high specific activity.

**Table 3. Typical fission product iodine content of a typical 20-MW(t) reactor at shutdown**

Iodine isotope	Half-life ( $t_{1/2}$ )	Specific activity (Ci/g)	Core inventory at shutdown for 20-MW(t) reactor operated 300 d (Ci)	Total iodine mass at shutdown (mg)
127	stable			9,720
128	25.0 min	$5.87 \times 10^7$	$1.80 \times 10^2$	~0
129	$1.7 \times 10^7$ years	$1.7 \times 10^{-4}$	$5.61 \times 10^{-3}$	32,500
130	12.4 h	$2.0 \times 10^6$	$3.03 \times 10^3$	2
131	8.05 d	$1.24 \times 10^5$	$5.64 \times 10^5$	4,560
132	2.3 h	$1.03 \times 10^7$	$7.96 \times 10^5$	77
133	21.0 h	$1.12 \times 10^6$	$1.02 \times 10^6$	904
134	53.0 min	$2.65 \times 10^7$	$1.28 \times 10^6$	48
135	6.7 h	$3.47 \times 10^6$	$1.08 \times 10^6$	313
136	83.0 s	$1.0 \times 10^9$	$4.61 \times 10^5$	~0
137	23.0 s	$>10^9$	$8.39 \times 10^5$	~0
138	5.9 s	$>10^9$	$5.92 \times 10^5$	~0
139	7.0 s	$>10^9$	$2.97 \times 10^5$	~0
Totals			$7.928 \times 10^6$ Ci	48,126 mg

Source: Craig, 1970.



2. Iodine-129 ( $t_{1/2} = 1.7 \times 10^7$  years) and  $^{127}\text{I}$  (stable) make up the major fraction ( $\sim 87\%$ ) (Craig et al., 1970) of the fission product iodine. The bulk of these isotopes must be taken into account when designing filters for both power stations and reprocessing plants. One of the factors that make  $^{129}\text{I}$  a potential hazard is that because it is a low beta and gamma energy emitter, detection and measurement are difficult.

While the primary form of iodine in the DOG is  $\text{I}_2$ , it is expected that at least some portion of the iodine atoms will react with other compounds found in the process lines to form other iodine species. A high proportion of organics and organic iodide compounds in the VOG can be expected. The following species have been identified or are postulated to be present:

- I and  $\text{I}_2$
- HI
- HOI
- ICN
- $\text{CH}_3\text{I}$
- Higher alkyl iodides, up to octyl iodide
- Aromatic iodides

#### 4.2 ORIGIN OF ORGANIC IODIDES

The formation of organic iodides in significant quantities is not too surprising considering the tendency of trace quantities of gaseous iodine to react with organic compounds in the environment. Burger (1958) proposed that the primary route for the formation of organic iodides is via the reaction of iodine with alkyl radicals from radiolysis in the dissolver. The alkyl radicals may arise from traces of oil on the sheared fuel, from the organic used in solvent extraction and recycled with the nitric acid, or from residues of dioctyl phthalate (DOP) used in leak testing.

The simplest organic iodine compound is methyl iodide ( $\text{CH}_3\text{I}$ ), which is formed by the reaction of iodine and small quantities of methane ( $4.5 \times 10^{-8}$  m/L) always present in the air (Parsly, 1971). Methyl iodine was identified as early as 1963 (Atkins and Eagleton, 1963) during tests in room air following the release of elemental iodine. Subsequently, this compound was also identified in the room and exhaust air and in the off-gases from reactors. The concentration of iodine in the dissolver of a fuel reprocessing plant is about 0.0007 M, and some lesser concentration of organics is also observed (Hebel and Cottone, 1982). A typical figure of 10% conversion to organic iodides could be explained by reaction with organic compounds at a concentration of 0.00007 M. The level of organic contamination in the dissolver can be reduced by reducing the quantity of organic impurities in the recycled nitric acid fed to the dissolver.

Parsly (1971) has prepared an in-depth summary of the chemical and physical properties of  $\text{CH}_3\text{I}$ . Parsly has examined the work of Golden and Walsh, and Benson, Goy, and Pritchard (who published their results almost simultaneously) on the equilibrium of



The attainment of equilibrium is slow, requiring several hours. Because a major portion of the observations by other investigators occurred at temperatures greater than 400°C, these observations are of little significance in off-gas handling.

Parsly (1971) also examined studies of radiation effects on  $\text{CH}_3\text{I}$ . These effects fall into two major categories: photolysis and radiolysis. The literature to be found on radiolysis is quite extensive; however much of the information concerns the liquid phase. Tang and Castleman (1968a, 1968b, and 1970) indicate that the rate of decomposition of  $\text{CH}_3\text{I}$  in air is a function of the dose to the air and the initial  $\text{CH}_3\text{I}$  concentration. Concentrations of  $10^{-8}$  to  $10^{-6}$  mol of  $\text{CH}_3\text{I}$  per liter of air were reduced by a factor of 10 by a dose of  $5 \times 10^5$  rads. It also appeared that water vapor hindered the decomposition.

### 4.3 HYPOIODOUS ACID

Iodine undergoes hydrolysis in aqueous solutions to form hypoiodous acid (HOI) according to



The existence of airborne HOI in a steam/air atmosphere was first postulated in 1968 by Keller et al. of Idaho Nuclear Corporation (Cartan et al., 1968). Numerous investigators (Browning, 1964; Chamberlain et al., 1963; Nakhutin et al., 1969) have observed an iodine compound (neither elemental nor organic) in a humid atmosphere.

Although HOI appears to have a long half-life in air, about 0.5 d, there is no proof that it exists as a gaseous component or as a stable airborne species. There are, however, several reactions that indirectly indicate its presence in off-gas and exhaust air streams.

Experiments by Keller et al. (1970) have shown that the optimum conditions for the formation of HOI are in iodine concentration in liquid of approximately  $10^{-6}$  M, a pH of 10, and a temperature of 90°C. Kabat (1974) has also presented the results of an extensive study of the relations and kinetics for the production of HOI.

### 4.4 HYDROGEN IODIDE

Another inorganic form of iodine that may need to be considered is hydrogen iodide (HI), which is expected to occur only under reducing conditions (Wilhelm, 1977).



## 5. REMOVAL METHODS

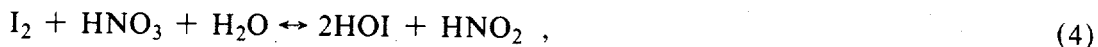
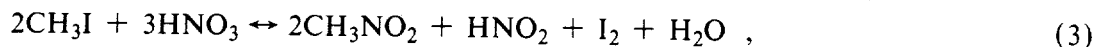
During the past two decades, various systems have been studied to reduce the iodine released to the environment. Three liquid scrubber systems are currently available: the Iodex system, the mercuric nitrate-nitric acid (Mercurex) system, and caustic scrubbers. Solid sorbents have also been studied, either as secondary systems to provide final filtering following use of the liquid scrubbing techniques or as primary systems to replace the liquid methods. These solid sorbents include silver faujasite, silver mordenite, alumina silicates, and macroreticular resins. Activated carbons have also been examined as a reference material. However, activated carbon cannot be considered as a primary sorbent for the treatment of reprocessing plant off-gas because of its low ignition temperature and its adverse reactions with nitrogen oxide which could lead to the formation of explosive compounds and to poisoning by organic contaminants in the off-gas.

### 5.1 LIQUID SCRUBBING METHODS

#### 5.1.1 Iodex Process

If very high DFs are required, one of the more promising systems, to date, for primary iodine removal is the Iodex system. Otherwise, solid-sorbent-based processes tend to be favored. The Iodex system has been tested on an engineering scale and has demonstrated good capabilities and operability. DFs in excess of  $10^6$  have been obtained. There are, however, concerns about the long-term integrity of the materials of construction that come in contact with the 20 to 23 M  $\text{HNO}_3$  scrub solution.

The Iodex process involves passing the DOG or VOG streams through 20 to 22 M  $\text{HNO}_3$  in a bubble-cap column. The process has been described in Energy Research and Development Agency (ERDA)-76-43 (1976). The solution chemistry involves the reactions:



Other organic iodides are expected to react in the same way as  $\text{CH}_3\text{I}$ .

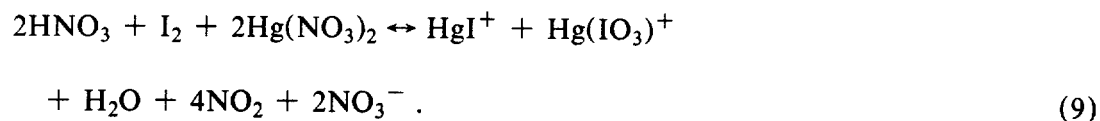
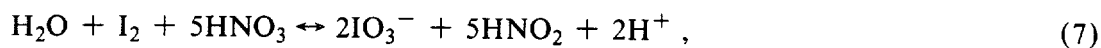
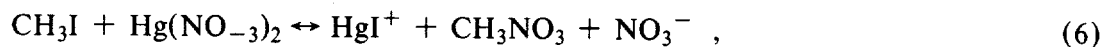
For gas velocities in the range of 30 m/min, methyl iodide DFs of 2–3 per plate have been obtained for bubble cap columns of conventional design. The DF varies inversely with the gas velocity. Elemental iodine DFs are normally twice those for methyl iodide. The process is not sensitive to the countercurrent liquid flow provided that the acid concentration is maintained above 20 M and that the solubility of the anhydroiodic acid  $\text{HI}_3\text{O}_8$  is not exceeded (1.4 g/L in 20 M  $\text{HNO}_3$  at 25°C). The iodine product is obtained by evaporating the nitric acid from the liquid effluent from the bottom of the bubble cap column. This results in a solid iodine product. This solid product is, however, water soluble and must undergo further treatment prior to final disposal. The nitric acid evaporated from the column bottoms can either be used as makeup acid in the reprocessing plant or it must be reconcentrated before it is recycled to the Iodex column. The reconcentration of the nitric acid is achieved by extractive distillation using magnesium nitrate to permit the production of hyperazeotropic acid.

By concentrating  $\text{HI}_3\text{O}_8$  to the solid form, the halogen waste volume from a 1,500-t/year FRP would be about 0.3 m<sup>3</sup>/year for a yearly inventory of 340 kg of <sup>129</sup>I, <sup>127</sup>I, and <sup>81</sup>Br [IAEA, to be published (b)]. The use of cement for immobilizing iodine waste for the Iodex process has been investigated (ERDA, 1976). Up to 9 wt % of iodine can be incorporated in a cement matrix as barium iodate. About 3 m<sup>3</sup> of cement would be required to immobilize the 340 kg of halogen fission products.

It is anticipated that the Iodex process equipment would be fabricated from tantalum. Zircaloy is subject to stress corrosion cracking in nitric acid at concentrations greater than 20 wt % (Beavers et al., 1981). Welded joints would be particularly sensitive to corrosion.

### 5.1.2 Mercurex Process

In the Mercurex process, the iodine is absorbed in a  $\text{Hg}(\text{NO}_3)_2\text{-HNO}_3$  solution and converted to iodates and mercury complexes via the reactions:



The scrub solution is 8–12 M  $\text{HNO}_3$  and 0.2–0.4 M  $\text{Hg}(\text{NO}_3)_2$ . The gas stream is passed through a packed-bed scrubber through which the solution is recirculated. The

iodine loading of the waste stream is typically 1 mol of iodine per 4 mol of mercury; thus, the effluent steam from the Mercurex process installed in a 5-t/d FRP might consist of 100 L/d of solution containing 1,300 g of  $^{129}\text{I}$  (ERDA, 1976). This would amount to about 30 m<sup>3</sup>/year of liquid waste. The operating conditions for application of the Mercurex process in the now closed Allied-General Nuclear Services (AGNS)-FRP are provided in the AGNS Safety Analysis Report (AGNS, 1973). In this facility two iodine scrubbers would have been used. The first would scrub the DOG. The design capacity was 880 Nm<sup>3</sup>/h, with a contact time of 9 s, a solution temperature of about 40°C, and a pressure drop across the scrubber of 1,400 Pa (0.2 psi). The tower was 1 m in diameter and 7 m tall. The DOG consisted primarily of air in-leakage from the shear, which passed through the dissolver. The second scrubber was to treat the combined DOG, NO<sub>x</sub> scrubber off-gas, and the VOG streams. The designed capacity for this scrubber was 6,400 Nm<sup>3</sup>/h. The contact time was to have been 5 s, and the other conditions were identical to the DOG scrubber. The design DF was 10 or greater for each scrubber. The scrubber system was followed by two silver zeolite beds, each sized to provide a DF of 10. Thus, the overall DF for the DOG was to have been 10,000.

Testing at Oak Ridge National Laboratory (ORNL) by Finney et al. (1977) has shown DFs of up to 10<sup>4</sup> for elemental iodine and organic iodides under various operating conditions. DF's of up to 500 have been reported for tests conducted at the Association Studiecentrum Voor Kernenergie/Centre D'Etude de L'Energie Nucleaire-Belgonucllaire (SCK/CEN) for both elemental iodine and organic iodides (Broothaerts et al., 1976).

### 5.1.3. Caustic Scrubbing

Caustic scrubbing involves the conversion of elemental iodine to the iodide and iodate via the reactions:



Organic iodine compounds pass through this type of scrubber virtually unreacted. Carbon dioxide and NO<sub>x</sub> react in the scrubber to form carbonates and nitrates.

The caustic scrubbing solutions are generally recirculated through the scrubbing tower with a small makeup stream of fresh caustic to maintain acceptable caustic and carbonate concentrations. A side stream is also generally withdrawn which contains the iodides and iodates. The iodine containing species are, for the most part, only minor constituents, and the process is generally limited by the solubility of Na<sub>2</sub>CO<sub>3</sub> if NaOH is used. Variations to the process have been proposed to overcome the problems of sodium by replacement of potassium hydroxide because the carbonate form is more soluble. Waste volumes are generally controlled by the production of carbonate arising from the CO<sub>2</sub> in the off-gas stream. The treatment of a 170-m<sup>3</sup>/h off-gas stream would produce about 38 m<sup>3</sup>/year of waste solution (Bray et al., 1977). The  $^{129}\text{I}$  waste generated by caustic scrubbing in the

U.K. Windscale-FRP has been routinely discharged to the sea, and similar plans have been considered for the Japanese FRP. Table 4 from [IAEA, to be published (b)] provides a listing of the iodine removal methods used at various fuel reprocessing plants worldwide.

#### 5.1.4 Electrolytic Scrubbing

This process uses  $\text{Co(III)}$  in 8 M  $\text{HNO}_3$  to trap iodine (Mailen and Horner, 1976). The  $\text{Co(III)}$  concentration is maintained by an electric current passing through the solution. The process solution is then evaporated, resulting in a solid mixture of cobalt nitrate and periodate. The small bulk of the iodine-containing solid is an attractive feature of this process. The iodine product is suitable for temporary storage or for conversion to a more stable form. The process has, however, lost favor after limited investigation and appears to have been abandoned.

### 5.2 SOLID SORBENTS

In comparison to the liquid systems, solid sorbents offer a much simpler iodine removal scheme in a number of aspects:

1. They allow for a simpler removal system design.
2. They are comparatively noncorrosive.
3. The waste produced is in a dry form that is easy to handle and contain.
4. The simpler system design, with few moving parts, makes for higher reliability and lower maintenance costs.

A variety of solid sorbents have been examined over the past two decades. The most widely studied are carbon adsorbents. These pose certain problems in a reprocessing plant environment, and, as a result, silver-containing adsorbents have gained in favor. The silver-containing sorbents fall into several classes: (1) silver reactors, (2) silver-exchanged zeolites, and (3) silver-impregnated silica. In addition, other metals have been examined, and various resins have been evaluated. In general, iodine DFs are limited to about  $10^3$ , and significant operating costs can be expected, particularly if the silver is not recovered. In the past few years, regenerable adsorbents have also received considerable attention.

#### 5.2.1 Activated Carbon

Of the solid sorbents proposed for iodine removal, activated carbon has been the most widely studied. Currently, nuclear power plants almost exclusively use impregnated, activated carbon for the removal of radioiodine. It was discovered that impregnation is required to remove  $\text{CH}_3\text{I}$  from high-humidity gas streams; the most widely used impregnates currently are  $\text{I}^-$ ,  $\text{KI}$  and triethylenediamine (TEDA). The removal of radioiodine from gas streams by activated carbon appears to be a function of many variables. Because

Table 4. Off-gas cleaning systems for  $^{129}\text{I}$  in FRPs

	Capacity (t/d)	Percent of I in DOG	I-trapping systems	DFs	
				Trap	Overall to stack
<b>Metal fuel plants</b>					
Purex, Hanford	10	80%	Caustic scrub Silver reactor	NR <sup>a</sup> 200	NR
TBP, Windscale (1964 results)	5	5%	Caustic scrub	50	1000 currently 20-30
UP <sub>2</sub> , La Hague	4	99%	Caustic scrub	NR	20
DFR, Dounreay	Small	95%	Mercurex	150	
<b>Oxide fuel plants</b>					
NFS, West Valley (closed down)	1	25%	None		4
WAK, Karlsruhe	0.2	99%	AC 6120	10 <sup>4</sup>	200
HAO, La Lague	2	NR	Caustic scrub	NR	50
PNC, Tokai Mura	1	99%	Caustic scrub Silver faujasite	NR NR	200
Eurex, Saluggia (combined metal and oxide plant)	Small	High	Nitric scrub Silver faujasite	NR NR	200
<b>Estimates only, not performance figures:</b>					
NFS, West Valley (proposal, never implemented)	2.5	90%	Mercurex Caustic scrub Silver mordenite	32 1 <sup>b</sup> 100	3500
AGNS, Barnwell (never operated)	5	98.8%	Mercurex Silver faujasite	10 100	1000
THORP, Windscale (planned)	5	High	Caustic scrub Possibly AC 6120	NR NR	NR

<sup>a</sup>NR = not reported.<sup>b</sup>Caustic scrubbing for HNO<sub>3</sub> vapors from Mercurex process and to protect silver Mordenite.

Source: IAEA, to be published (b).



of worldwide interest in this material for reactor ventilation applications, numerous reports and papers have been published which deal with iodine removal as affected by the following parameters: inlet iodine concentration, relative humidity, bed temperature, service time and weathering, radiation, impregnation, manufacture, particle size, and gas velocity through the filter.

Although activated carbon has been successfully used in power plants, it has several serious drawbacks.

1. It has a relatively low ignition point; thus, without continuous air flow through the filter, the decay heat of trapped radioiodine could ignite the bed, especially in the processing of short-cooled fuels.
2. The bed has poor iodine retention at high temperatures and permits total iodine release upon ignition.
3. The presence of nitrogen oxides adversely affects the bed's performance; nitrogen oxides can also lead to the formation of explosive compounds within the filter bed (Pence, Duce, and Maeck, 1972a; Evans and Jones, 1972).

These factors virtually rule out the use of this material in reprocessing plant off-gas systems.

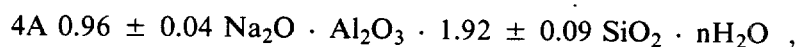
### 5.2.2 Zeolites

Carbon filters have certain disadvantages: iodine desorption at relatively low temperatures, low ignition temperature, possible buildup of explosive gases, and poor performance in a steam environment. A more promising approach to the problem of iodine removal is the use of inorganic adsorbers in which a stable iodine compound is formed. An initial scoping study was performed by Maeck, Pence, and Keller (1968) in which 25 materials were tested for  $I_2$  and  $CH_3I$  retention. Based on this study, a synthetic zeolite, Linde molecular sieve 13X, converted to the silver form (AgX) was selected as the most promising of the materials tested.

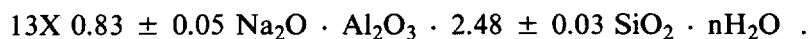
The advantages that AgX has over activated carbon are that (1) it is nonflammable, (2) it operates well at elevated temperatures, (3) it poses no explosion hazard, (4) it is resistant to poisoning, and (5) it forms an insoluble iodine product.

#### 5.2.2.1 Zeolite structure

Different types of zeolites have varying physical properties. One of the most important properties is the  $SiO_2:Al_2O_3$  ratio. The higher this ratio, the harder the material, the more acid resistant the zeolite, and the lower the ion-exchange capability. Hersh (1961) reports the chemical formula of Linde's synthetic zeolites are:



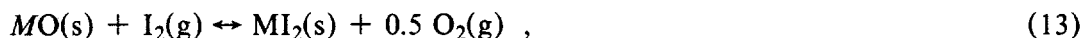
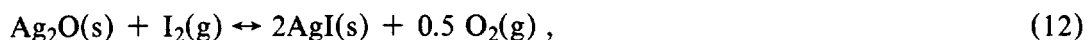
5A similar to 4A 75% Na replaced with Ca ,



The sodium in the zeolite structure can be exchanged for other metal cations. A batch method for silver exchange is presented by Pence, Duce, and Maeck (1970a, 1970b) and both batch and plug flow techniques are described by Thomas et al. (1977).

#### 5.2.2.2 Chemical mechanisms

The exact mechanism for iodine sorption on metal-exchanged zeolites has not yet been determined. Physisorption and chemisorption are the two mechanisms that Thomas et al. (1977) proposed as responsible for iodine adsorption. The degree to which each of these occurs depends on the type of metal exchange zeolite used (Table 5). If one assumes that the metal ions exist as oxides in the zeolite structure, the reaction could be:



where

$M = Pb \text{ or } Cd$ .

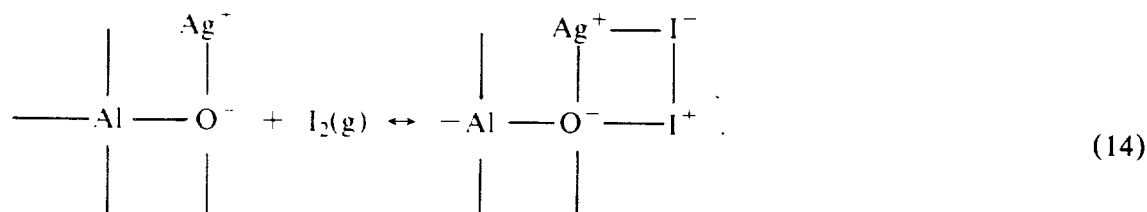
**Table 5. Maximum iodine adsorption capacities (magnesium of  $I_2$  per gram of bed)<sup>a</sup> of metal zeolites at 150°C**

Adsorbent	Saturated	Physisorbed	Chemisorbed
NaX	364	334	30
AgX	349	135	214
PbX	179	153	26
CdX	374	329	45

<sup>a</sup>Based on dry weights of 0.61 g/cm<sup>3</sup> for NaX, 0.71 g/cm<sup>3</sup> for CdX, and 0.85 g/cm<sup>3</sup> for PbX and AgX.

Source: Thomas, 1977.

The standard free energies at 25°C of the reactions are 18.6, 0.6, and 2.65 kcal/mol of  $I_2$  for silver, palladium, and cadmium, respectively. For copper, cobalt, iron, nickel, and zinc, the oxides have free energies of reaction of 20 kcal/mol or more. It is evident that all the previous metal oxides, with the exception of silver, are more stable in their oxide form, which accounts for the large chemisorption capacity of AgX. A plausible mechanism for the reaction might be:



### 5.2.2.3 Use of alternative metal-exchanged zeolites

Because of the high cost of silver, alternate methods using zeolites have been examined to reduce the cost of the metal-exchanged zeolite iodine filter unit. First, other metal cations were exchanged; next, the silver content was reduced; finally, a method for filter bed regeneration was developed.

Work by Adams et al. as reported by Unger et al. (1970a) on zeolites treated with  $CrCl_2$ ,  $Pb(NO_3)_2$ , and  $Mn(NO_3)_2$  solutions gave  $CH_3I$  trapping efficiencies at 200°C of 6, 32, and 68%, respectively, for loadings of 0.5 mg  $CH_3I/cm^3$  sorbent on a 2-in. deep bed. Studies were also performed on cadmium and potassium zeolite at 200°C at higher loadings. These efficiencies decreased rapidly as loadings were increased to 37 mg/cm<sup>3</sup>; the limit of chemisorption had been reached at this loading. The idea of a mixed bed of AgX and another metal-exchanged zeolite to extend the useful life of the more costly silver zeolite was also proposed.

Maeck and Pence (1970) studied lead-exchanged zeolite and found that while PbX had a low removal efficiency for  $CH_3I$ , more than 97% of elemental iodine was removed from air at 21°C and 90% relative humidity at bed temperatures above 45°C.

Later work by Pence, Duce, and Maeck (1972b) examined additional metal cation-exchanged zeolites: cadmium, copper, mercury, palladium, thallium, and some rare earth cations. Some showed promise for elemental iodine removal, but efficiency decreased markedly with increasing relative humidity at a fixed temperature. However, in spite of the increase in water content in the air, the adsorption efficiencies increased as the bed temperature was increased from 22 to 90°C at fixed relative humidity. The mercuric ion-exchanged Y-type zeolite,  $Hg^{2+}Y$ , showed the best efficiency of all zeolites tested other than silver. It was capable of removing more than 99.9% of the  $I_2$  from a water-saturated air stream at 22°C. For  $CH_3I$ , the efficiency of the metal-exchanged zeolites, except silver, decreased significantly. The highest was  $Hg^{2+}Y$  with a removal efficiency of 33.8% at 125°C and 90% relative humidity. The PbX also showed some promise in a heated bed for  $CH_3I$  removal.

Thomas et al. (1977) also examined metal-substituted zeolites. Cadmium and palladium were effective up to loadings of 3.5 mg of  $I_2$  per gram of substrate, but copper and

zinc zeolites were found ineffective. Studies with the sodium form of the zeolite indicated that it was the substrate that traps the iodine and not the palladium or cadmium. Silver-exchanged zeolites, however, gave removal efficiencies of 99.5% at loadings up to 190 mg of  $I_2$  per gram of substrate.

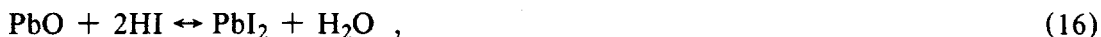
Somewhat more limited work has been done on partial exchange of silver for sodium to reduce the filter cost. Pence, Duce, and Maeck (1972b) reported that the adsorption efficiency of AgX in a high-humidity environment was quite sensitive to the extent of silver exchange.

#### 5.2.2.4 Regeneration of AgX

After limited success in attempts to develop an alternate metal-exchanged zeolite to replace the costly silver form, studies were undertaken to find a method to regenerate the filter bed. Work at Idaho National Engineering Laboratory (INEL) (Thomas et al., 1977, Slansky et al., 1976a) showed that regeneration using high temperature (400 to 500°C) hydrogen was possible. A flow plan of the process is shown in Fig. 1. The proposed reaction is:



with the HI produced being chemisorbed on lead zeolite. While the chemisorption of  $I_2$  in PbX is not thermodynamically favored, the reaction



has a free energy of reaction of  $-47$  kcal/mol at 150°C. It was reported that at a desorption temperature of 500°C, the AgX beds can be regenerated 10 times faster than the projected iodine adsorption rate.

Regeneration temperatures of 400 to 600°C have been tested. Little effect is noted between 400 and 500°C, however, there was a twofold loss in capacity of the AgX after five cycles at both temperatures. After three cycles at 600°C, there was a threefold decrease in capacity, which was attributed to pore collapse within the zeolite structure; therefore, a limit of 500°C is recommended for zeolite regeneration.

The iodine removed from the AgX bed was chemisorbed onto lead as  $PbI_2$  loadings to 88% utilization of the lead ( $\sim 389$  mg of  $I_2$  per gram of PbX) have been obtained. A bright-yellow compound,  $PbI_2$ , has a solubility in water of 26 mg of  $I_2$  per 100 mL of water at room temperature.

Work by Burger (1977) was directed toward the fixation of HI in bismuth and copper solutions. Copper solutions required the introduction of  $SO_2$  to prevent the carry through of  $I_2$  from the reactions:

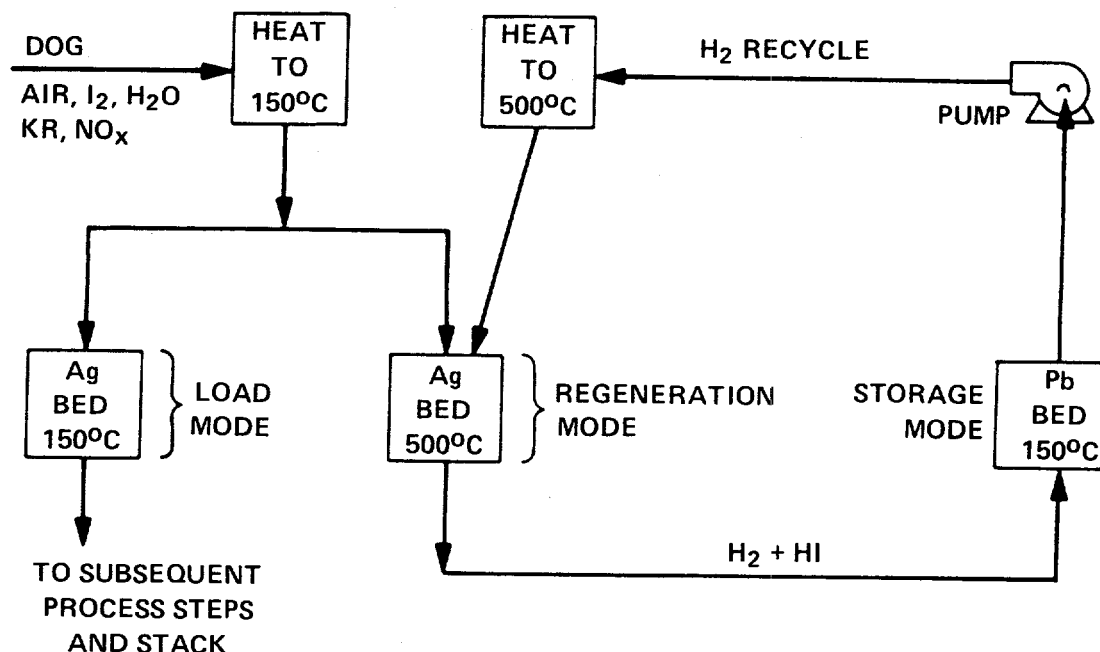


Fig. 1. Zeolite regeneration flowsheet.



Bismuth solutions were then employed to avoid the reoxidation problems of the copper solution. The final product  $\text{BiI}_3$  was a fine, dense, black precipitate. A problem associated with this process was that  $\text{BiI}_3$ , in some cases, held excess  $\text{I}_2$ , which was volatilized upon heating.

Early work by S.C.K./C.E.N. (Broothaerts et al., 1973) indicated that nonexchanged zeolites could be regenerated five times at 200°C with no effect on capacity. No mention was made of the exact method of regeneration or the medium for final iodine trapping.

### 5.2.2.5 Poisoning of AgX

The effects of various contaminants have been studied by several workers. The *Nuclear Air Cleaning Handbook* (Burchsted, Fuller, and Kahn, 1977) indicates states that HCl vapor seriously degrades zeolite trapping efficiency. Pence, Duce, and Maeck (1972b) examined the effects of several gases on the methyl iodide removal efficiency of silver zeolites. Of the gases studied, only  $\text{H}_2\text{S}$  and  $\text{SO}_2$  had serious effects. Small adverse effects were noted for both  $\text{NO}_2$  and propane; however, these studies were carried out under abnormally high contaminant gas concentrations.

Work by Thomas et al. (1977) indicated a threefold decrease in  $I_2$  loading on AgX in the presence of 2%  $NO_2$ . Also noted was the interaction of water vapor with  $NO_2$ .

#### 5.2.2.6 Relative humidity

The effects of relative humidity have been studied by numerous researchers, and consistent results have been obtained. While there was a decrease in efficiency with increased humidity, the adverse effects were far less for AgX than for carbon. The decrease in efficiency was also less at higher temperatures. For a fixed relative humidity,  $CH_3I$  adsorption increased with temperature (Maeck and Pence, 1970).

Shiomi et al. (1983) provide a parametric study of charcoal and AgX iodine removal efficiencies at relatively low temperatures. From the experimental data and mass transfer theory, an experimental equation for evaluating the removal efficiency was derived which accounts for temperature, relative humidity, face velocity, and preflow conditioning.

#### 5.2.2.7 Process capacity

Obtaining the maximum operational process capacity of silver zeolite is an almost impossible task because of the number of variables concerned. The maximum theoretical capacity is 1,192 mg of  $I_2$  per gram of silver, and at 100% exchange of silver for sodium, the silver would compose 36% (Thomas et al., 1977) of the structure; therefore, the maximum loading per gram of silver zeolite would be 429 mg of  $I_2$ . There have been many test runs at low loadings ( $<10$  mg of  $I_2$  per gram of AgX), and DFs have been obtained ranging from  $10^2$  to  $10^5$ .

Pence, Duce, and Maeck (1970b) showed that a DF of  $10^4$  was possible for  $I_2$  removal at  $22^\circ C$  on a 5.08-cm deep bed with a gas velocity of 92 ft/min under 100% relative-humidity conditions. The gas concentration was 1 to 10  $\mu g$  of  $I_2$  per cubic meter.

#### 5.2.2.8 Operational experience

McDaniel and White (1981) describe the rationale used to justify the use of AgX as the iodine-adsorption medium in the filtration system for the loss-of-fluid-test (LOFT) containment vessel atmosphere cleanup system. The system was designed to process 8,000 cfm of containment vessel gas. The design used a gasketless adsorber unit to contain the AgX sorbent material. Cost studies indicated AgX initial costs were about 10% higher than carbon because of the costs of the fire detection and suppression equipment. Tests on the iodine removal efficiency during the first two years of operation indicated  $>99.94\%$  for  $CH_3I$ . No data were presented on the iodine loading achieved during the observation period. There were no indications of any degradation during the 1,000 h of operation in the two-year period.

AgX iodine adsorbers were installed in the Tokai reprocessing plant beginning in 1979 (Kikuchi, Omori, and Takeda, 1985). One adsorber unit was installed in the main plant, and three additional units were installed in the waste disposal facility. The main plant

filter unit processes the off-gas from the shear, dissolver, high-level liquid waste system, and the VOG system. Prior to the AgX trap, all off-gas is routed through an alkaline scrubber. The major iodine burden is removed from the dissolution off-gas by the caustic scrubber; however, the caustic scrub on the VOG stream is not nearly as effective, probably because of the higher level of organic iodides in this stream. The overall DFs for the main plant have been maintained at 100 or better.

The current AgX filters are operated at  $<50^{\circ}\text{C}$ . Considerable loss in iodine removal efficiency was observed in the filters installed in the waste facility which are exposed to high levels of  $\text{NO}_x$ . The DF across the AgX beds were very low, ranging from 10 to 70. This is probably because of the low operating temperature. The current bed design uses 5-cm-deep beds with a face velocity of 5 cm/s. New off-gas system designs specify operation of the AgX filters at  $150^{\circ}\text{C}$  and at a face velocity of 20 cm/s.

### 5.2.2.9 Advantages and disadvantages

Silver zeolite can be used in a wide range of operating conditions with excellent results for  $\text{CH}_3\text{I}$  and  $\text{I}_2$  removal. Its advantages can be summarized as:

1. Low flammability.
2. Low explosion hazard.
3. Final silver zeolite-iodine complex is a solid for final storage.
4. Removal efficiency increases with temperature and shows efficient sorption to  $500^{\circ}\text{C}$ .
5. High temperature (up to  $1,000^{\circ}\text{C}$ ) is retained.
6. Removal of elemental iodine is not affected by many contaminants.
7. High capacity exists for  $\text{CH}_3\text{I}$ .

Silver zeolite also has the following disadvantages:

1. The cost of silver makes the product about 20 times as expensive as carbon.
2. X-type zeolites are not acid resistant and are also affected by prolonged exposure to steam.
3.  $\text{CH}_3\text{I}$  removal is affected by  $\text{SO}_2$ ;  $\text{H}_2\text{S}$ ; and, to some degree,  $\text{C}_3\text{H}_8$  and  $\text{NO}_2$ .

### 5.2.3 Mordenites

The use of silver-exchanged mordenites began as an extension of the metal-exchanged zeolite developmental work. Silver-exchanged adsorbents appeared well suited for bulk iodine removal, except that their high cost would make on-time use almost prohibitive on a large scale. As a result, other less expensive metal-substituted zeolites were examined to

determine their usefulness in iodine removal. These zeolites proved ineffective, and developmental work on a method of regeneration for silver sorbents was begun. One of the primary objectives of the work with mordenites was to identify a substrate that has high thermal stability and that would retain its iodine-removal capacity after multiple cycles.

As mentioned previously, silver zeolite lost about 50% of its iodine capacity after five regenerations and was also adversely affected by acid vapors. Literature from Norton Company (Norton, 1976) indicated that zeolon molecular sieve material has superior acid-resistant characteristics compared to X- and Y-type zeolites (Fig. 2).

Zeolons are a family of crystalline aluminosilicate compounds, both natural and synthetic, with extremely uniform pore openings and a high  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio. The high  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio of 10 is indicative of high chemical stability. The precise structure of mordenites contrasts strongly with the wide pore-size spectrum found in conventional amorphous adsorbents such as silica gel, activated carbon, and activated alumina.

Zeolon 900 is a self-bonded synthetic mordenite. The lack of an added bonding agent is beneficial to its chemical stability. Zeolon 900 has the following chemical formula in the sodium form:

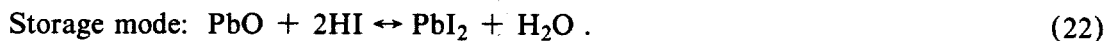
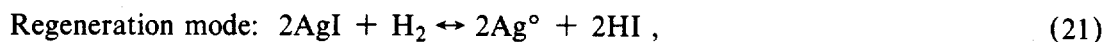


The effective pore diameter is reported by Norton to be 8 to 9A, and the material has a specific surface area of 400 to 450  $\text{m}^2/\text{g}$ .

### 5.2.3.1 Chemical mechanism

The chemical reactions that occur on the mordenite with elemental iodine and organic iodides have not been fully explained. However, it has been noted (Thomas et al., 1977) that the silver exists in both the ionic and metallic states. It also appears that the metallic state has a higher capacity than the ionic state for iodine chemisorption.

A proposed set of reactions for silver and iodine on mordenite is:



It was reported (Murphy, Staples, and Thomas, 1977) that NO had a positive influence on iodine loading. In the absence of NO,  $\text{NO}_2$  had a negative influence which may be due to the equilibrium reaction:



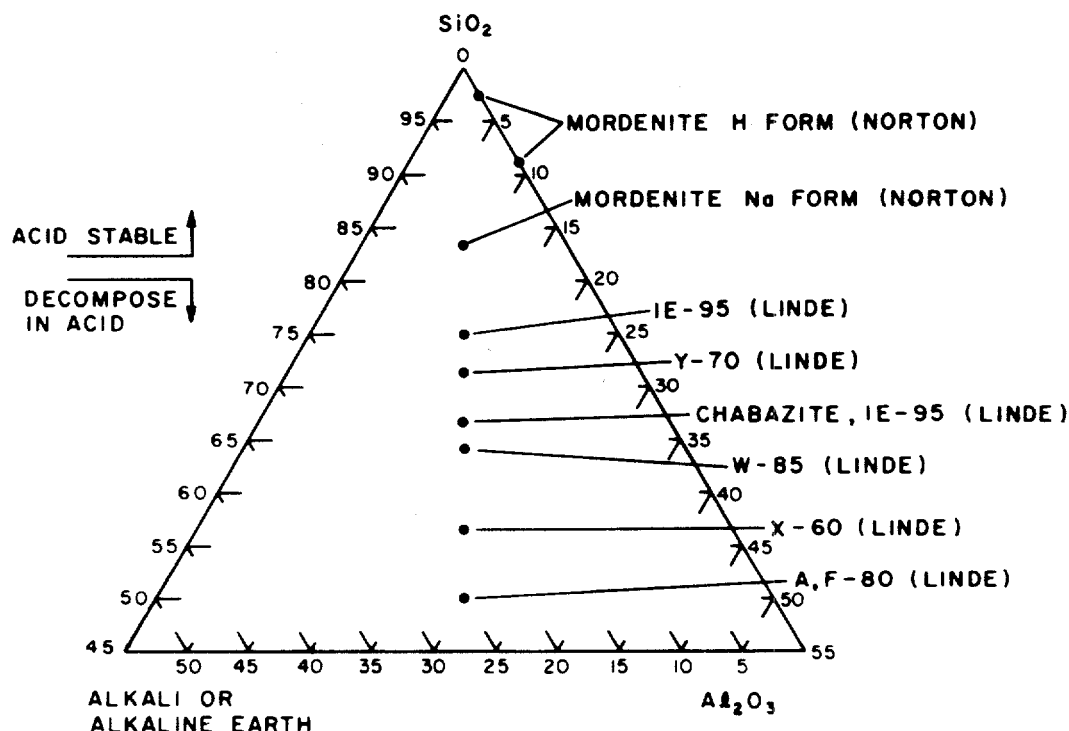
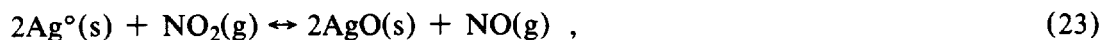


Fig. 2. Triangular diagram of zeolite composition.



Neglecting the effects of the mordenite matrix, the free energy of reaction to convert the metal to oxide is 6.3 kcal/mol at 150°C. This is thermodynamically unfavorable and would occur only in the absence of NO; NO also acts to hold silver in the metallic state even in the presence of  $\text{O}_2$ .

Extended purges of 16 to 64 h with dry air at 100°C resulted in a 60% decrease in the capacity of the silver mordenite (Thomas et al., 1977). The equilibrium reaction:



may be involved. At 180°C, the free energy of reaction to the oxide is zero. The addition of  $\text{H}_2$  could protonate the oxygen atom via the irreversible reaction:



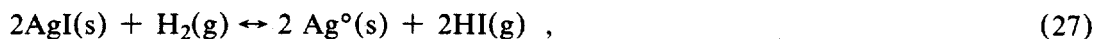
### Regeneration—Engineering Data and Experimental Results

The initial studies on silver mordenite at INEL were reported by Slansky et al. (1976a). This report indicated a 50% reduction in capacity of silver zeolite after 5 regenerations at 500°C with pure hydrogen, while at the same time, no reduction in iodine capacity was noted for silver-exchanged mordenite-zeolon 900 (AgZ). The regeneration method was the same as described earlier for AgX. In a slightly later report, Slansky et al. (1976b) indicate loadings of the AgZ of  $59.5 \pm 6.7$  mg I<sub>2</sub>/g AgZ (at 95% confidence level) with a DF of 250.

Desorption studies indicated that partial pressure of HI can be approximated by:

$$\log P_{HI} = -G^\circ / 4.6 RT, \quad (26)$$

for the reaction:



where

$P_{HI}$  = partial pressure of HI (atm) ,  
 $G^\circ$  = standard free energy of reaction ,  
 $R$  = ideal gas constant (1.98 cal/mol-°D) ,  
 $T$  = temperature (°K) .

The rate of desorption of HI from AgIZ was modeled by the second order equation:

$$Y = 0.585 + 0.456 X_1 + 0.477 X_2 + 0.064 X_1^2 + 0.0045 X_2^2 + 0.352 X_1 X_2, \quad (28)$$

where

$Y$  = mg HI/min-cm<sup>2</sup> ,  
 $X_1$  = [temp (°C) - 475]/75 ,  
 $X_2$  = [face velocity (cm/min) - 369]/246 .

The observed desorption rates agreed within  $\pm 11.1\%$  (at 95% confidence level) of the rates predicted.

Typical loading and regeneration operating conditions are shown in Table 6. The beds were first loaded with about 35 g of  $I_2$ , and then more than 99% of the iodine was stripped in each regeneration. Decontamination factors of  $10^4$  to  $10^5$  were achieved with loadings of 187 mg of  $I_2$  per gram of AgZ in the saturation zone of the bed.

Tests of the PbX beds indicated that loadings of 400 mg of iodine per gram of PbX were possible. The maximum loading for PbX is 400 mg of iodine per gram of PbX; thus, 90% of the lead was being used.

Table 6. Conditions for recycle tests on Ag°Z

Experimental variable	Iodine loading	Iodine stripping
Bed diameter, cm	5	5
Bed depth, cm	15	15
Particle size, mesh	10-20	10-20
Superficial face velocity, m/min	15	15
Bed temperature, °C	150	500
Inlet pressure, mm of Hg°	700	760
Carrier gas	air	hydrogen
Iodine concentration at 21°C and 1 atm, mg/m <sup>3</sup>	1500 <sup>a</sup>	7400
NO <sub>2</sub> concentration, %	2	0
NO concentration, %	2	0
Dew point, °C	35	nil
Iodine flux to and from bed, mg min <sup>-1</sup> cm <sup>-2</sup>	1.5 <sup>b</sup>	4.5

<sup>a</sup>Actual dissolver off-gas (DOG) concentration is anticipated to be about 300 mg of  $I_2$ /m<sup>3</sup>.

<sup>b</sup>Actual DOG iodine flux would be about 0.4 mg min<sup>-1</sup> cm<sup>-2</sup>.

Source: Murphy, Staples, and Thomas, 1977.

The final report on AgZ development from INEL (Murphy, Staples, and Thomas, 1977) reported that an AgZ bed had been loaded with  $I_2$  and recycled 13 times with a 20% loss in capacity compared to the initial loading (Fig. 3). The increased capacity on the second recycle was attributed to additional silver being exposed and reduced during the first regeneration. The progressive decrease in capacity was explained as a slow but steady pore collapse, which decreased accessibility to the silver atoms. It was also reported that silver oxide is not formed above 100°C in Ag°Z except by the reaction with NO<sub>2</sub> [Eq. (23)]; thus, no effect resulting from higher bed temperatures would be observed. Also noted was that other gaseous elemental halides should reduce the capacity of Ag°Z.

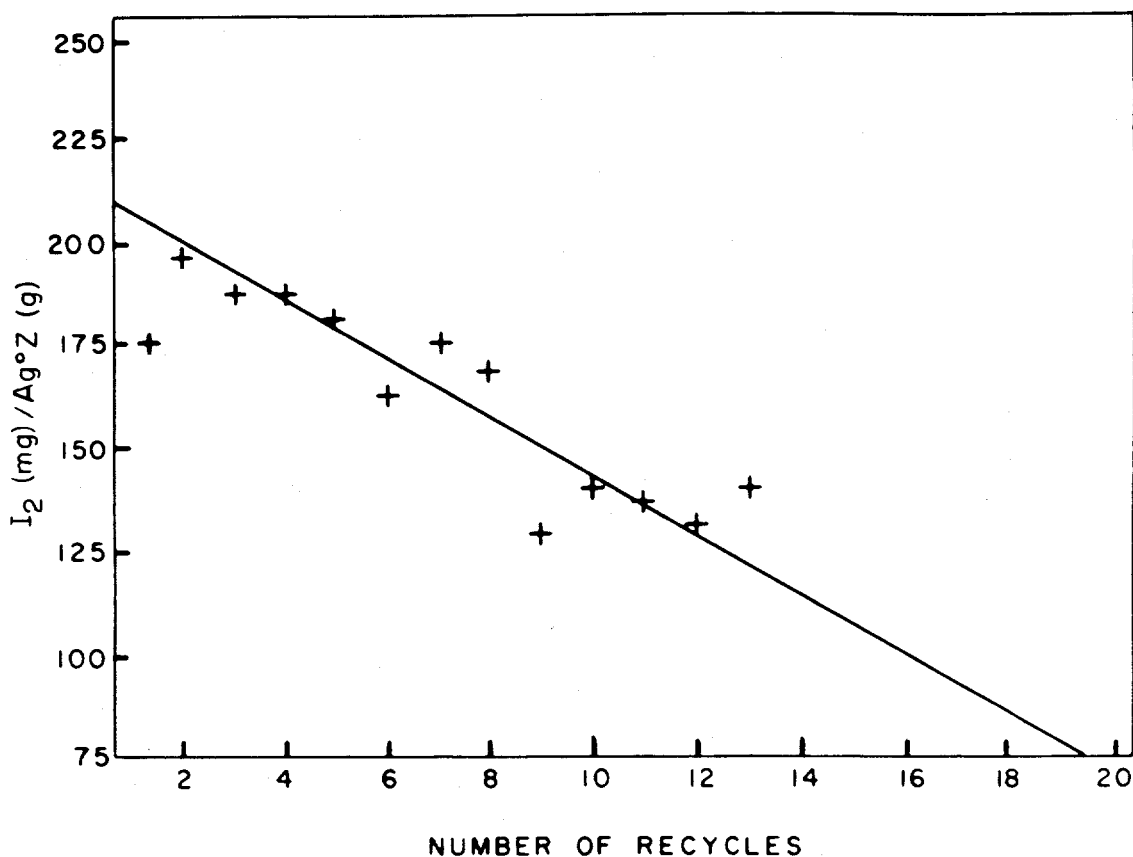


Fig. 3. Regeneration loading curve.

Tests of the regeneration potential of AgZ were conducted at ORNL (Jubin, 1981) to confirm the previously reported results. These tests were the first conducted in stainless steel filter housings and with dilute  $H_2$ . The 4.5 vol %  $H_2$  was chosen for safety reasons. More than 98% of the iodine loaded on the  $Ag^{\circ}Z$  as  $CH_3I$  was removed by the 4.5%  $H_2$ -95.5% Ar gas stream at 500°C. However, a dramatic loss in bed-loading capacity was observed following regeneration.

Following the pretreatment of AgZ with 4.5%  $H_2$ -95.5% Ar at 200°C, free silver was detected by X-ray diffraction. Prior to pretreatment with hydrogen, the free silver was not seen. A scanning electron micrograph showed nodules suspected to be free silver on the surface of the zeolite structure. Similar examination of AgZ prior to  $H_2$  pretreatment shows no such nodules. Photomicrograph measurements show the silver nodules to be on the order of 2000Å. The nodules were present on both the inside and outside surfaces of the pellet. They appeared to be attached to the major crystalline structure. Induced electron fluorescence indicated that additional silver (i.e., silver not present in the nodules) still remains attached to the mordenite structure. Similar results reported by Yates (1965) were further indications of the high mobility of the silver atoms.

Scanning electron micrographs of the regenerated  $\text{Ag}^\circ\text{Z}$  material showed extremely large ( $>8,000 \text{ \AA}$ ) silver nodules (Jubin, 1983). X-ray diffraction showed a much stronger silver band for the regenerated material than for the original  $\text{Ag}^\circ\text{Z}$ . The large number of silver nodules probably account for the reduced loading-capacity because the number of available silver sites are significantly reduced.

The effects of time and temperature on the formation of the silver nodules and the subsequent  $\text{CH}_3\text{I}$  loading were examined. A series of  $\text{Ag}^\circ\text{Z}$  beds were treated with 100%  $\text{H}_2$  for 24 to 48 h at temperatures of 200, 400, and  $500^\circ\text{C}$ . Following this treatment, the beds were loaded with  $\text{CH}_3\text{I}$  until the iodine DF dropped below  $10^3$ . The results of the bed loadings are shown in Table 7.

Loadings showed decreased retention capacity for  $\text{CH}_3\text{I}$  as exposure time to  $\text{H}_2$  increased and as temperature of the exposure increased. Photomicrographs showed small increases in the nodule size from 200 to  $400^\circ\text{C}$  and again a significant increase in the nodule size at  $500^\circ\text{C}$ .

Work by Burger and Scheele (1981) using a glass housing during the iodine loading and regeneration phases did not show the same large nodule formation following hydrogen pretreatment at  $500^\circ\text{C}$ . This study used a 320-g  $\text{AgZ}$  bed (5-cm diam  $\times$  20 cm), which was loaded and stripped a total of 12 times. The iodine loaded per cycle ranged from 60 to 125 mg of iodine per gram of  $\text{AgZ}$ , with an average of 86 mg of iodine per gram of  $\text{AgZ}$ .

During the bed drying and early stages of hydrogen treatment, considerable elemental iodine was released from the bed. This  $\text{I}_2$  was not captured by the lead zeolite bed but instead circulated throughout the recycle system or was deposited back onto the  $\text{AgZ}$  bed or various components of the system. This recycle of iodine caused considerable corrosion of the stainless steel components in the system.

**Table 7.  $\text{CH}_3\text{I}$  loadings of 100% hydrogen-treated  $\text{AgZ}$  in dry air**

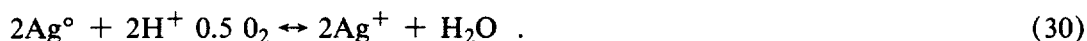
Run	Temperature ( $^\circ\text{C}$ )	Time (h)	Loading (mg/g)
57	200	24	35.6
58	200	48	12.3
59	400	24	11.0
61	400	48	8.0
60	500	48	0.26

Beginning with the fifth cycle of regeneration, the  $\text{AgZ}$  bed could no longer be completely stripped of iodine. The iodine accumulated with each successive cycle such that after regeneration 10 the bed contained 140 mg of iodine per gram of  $\text{AgZ}$ . Multiple stripping following loading 11 reduced the iodine content to 21 mg of iodine per gram of  $\text{AgZ}$ . It appeared that a regeneration temperature of  $550^\circ\text{C}$  was required to effectively strip the iodine.

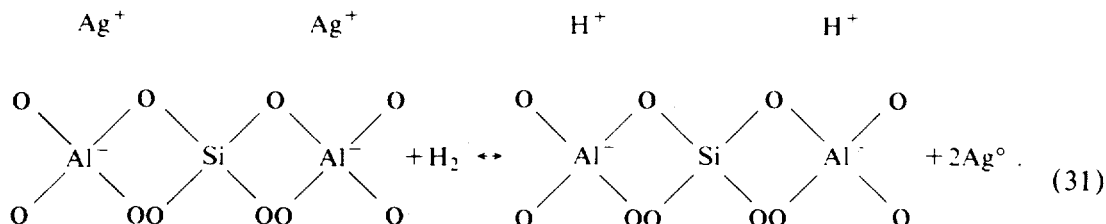
A series of tests were conducted by Jubin (1983) to explore the possible effects of housing material on postregeneration loading efficiency. AgZ was treated in a glass column with 100% H<sub>2</sub> for 24 h. The bed was then loaded with CH<sub>3</sub>I to 54 mg/g at 200°C in moist air. This loading is about half the loading observed for AgZ under the same conditions, but it was treated with 4.5% H<sub>2</sub> at 200°C and was 10 times more than loadings following hydrogen treatment at 500°C in stainless steel.

Beyer and Jacobs (1977) have also reported on the roles temperature and iron impurities play in the hydrogen reduction of AgZ. At increased reduction temperatures, the intensity of the (111) diffraction of crystalline silver external to the zeolite increases, and the particle size of the silver crystallites also increases. They also report that upon oxidation at sufficiently high temperatures, the external silver phase disappears. After a second redox cycle at 653K, a small amount of silver remains located between the zeolite crystallites, indicating a slight irreversibility of the system.

The proposed stoichiometry appears straightforward for both reduction and oxidation:



A second, and possibly clearer, representation of the reduction reaction showing the role of the mordenite is given by Tsutzuri and Takahashi (1977):



Beyer and Jacobs (1977) also indicated that the reduction is a catalyzed process where hydrogen is probably activated on iron impurities within the zeolite structure of the material they used. It was shown that the rate of reduction strongly depends on the iron content. In fact, using partially deironized material, the rate of reduction of silver ions showed a fivefold decrease, whereas the reduction mechanism remained unchanged as deduced from the slope of the Arrhenius plots.

This "activation" of the hydrogen by iron would account for the rapid formation of large silver nodules when treating AgZ in the stainless steel housing at high temperatures and the much slower formation of nodules in the glass housing. These reactions must be taken into account when designing actual plant off-gas systems using silver zeolites because it appears that the formation of the larger silver nodules severely limits the CH<sub>3</sub>I capacity of the AgZ.

### 5.2.3.2 Process capacity

The maximum theoretical loading of AgZ is 237 mg of  $I_2$  per gram of AgZ (Thomas et al., 1977). Loadings of 187 mg of  $I_2$  per gram of AgZ were regularly achieved in the saturation zone of the filter beds, which represents about 79% conversion of the silver. The average loading obtained for the bed was 100 to 130 mg of  $I_2$  per gram of AgZ. The maximum loads achieved on PbX have been  $\sim 400$  mg of  $I_2$  per gram of PbX, which was about 90% of the theoretical loading. Lead-exchanged mordenite (PbX) was also tested as a final disposal bed. PbZ has a maximum theoretical loading of 247 mg of HI per gram of PbZ as  $PbI_2$ ; however, loadings as high as 398 mg of HI per gram of PbZ have been reported (Murphy, Staples, and Thomas, 1977), which may have been the result of the formation of  $H_2PbI_4$ .

Later reports by Nichols et al. (reported in Slansky et al., 1977b) indicated the deleterious effect of a 16- to 64-h dry air purge at  $100^\circ\text{C}$ . This 60% decrease in loading capacity could be eliminated by the pretreatment of silver with  $H_2$ . Results also indicated that effects of the dry air purge could be alleviated by operating at  $150^\circ\text{C}$ .

The effects of temperature on the loading of  $CH_3I$  on  $Ag^+Z$  were examined by Jubin (1981). These studies indicated marked improvement in the loading capacity of the silver mordenite above  $150^\circ\text{C}$ . The loading tests were conducted in such a manner that the tests were terminated when the DF for the 4- to 6-in. filter bed fell below  $10^3$ . The maximum bed loading observed was 73 mg of  $CH_3I$  per gram of  $Ag^+Z$ . Minimal effects on loading were observed for  $NO$ ,  $NO_2$ , and  $CH_3I$  concentration.

### 5.2.3.3 Advantages and disadvantages

Mordenites have many of the same characteristics and advantages of zeolites. In addition to those, mordenites also have the following characteristics:

1. The capacity for  $I_2$  is improved by the presence of  $NO$  in the gas stream.
2. They have a high recycle capability; up to 13 recycles with only a 20% reduction in loading capacity.
3. They are more acid resistant than zeolites.
4. The adverse effects of 2%  $NO_2$  and/or 6%  $H_2O$  is negated by 2%  $NO$  in the gas streams.

The following disadvantages primarily indicate a lack of information concerning the material rather than process disadvantages.

1. The cost of silver is high.
2. The complete life cycle of regenerated AgZ material is not known and varies from researcher to researcher (i.e., no more than 13 recycles ever attempted).
3. No tests on extended temperature cycling have been made.
4. The effects of radiation on the material have not been examined.

5. Tests need to be performed to determine the effect of potential poisons to the filter bed.
6. Additional work is required to examine the proper storage medium for HI produced on regeneration if regeneration is elected.

#### 5.2.4 Partially Exchanged Silver Mordenite

Tests conducted at ORNL (Jubin, 1983) on fully exchanged AgZ indicated that the iodine probably first chemisorbs at the silver sites most accessible. In addition, experience in exchanging the sodium for silver has also shown that the last 25% of the exchange was the most difficult to complete. Tests were conducted to determine the effects of NO, NO<sub>2</sub> humidity, bed temperature, dilute hydrogen, and silver content. The dilute hydrogen was added during some loading tests in an attempt to maintain the silver in a reduced state during the loading phase.

Results of the testing indicated that:

1. Increased CH<sub>3</sub>I loadings occur with increased silver content. This increase appears to stabilize above the 3% Ag content.
2. An operating temperature of 200°C is favored over either 150 or 250°C. The difference between 200°C loadings and 250°C loadings appears to decrease as the silver content increases. This corresponds to the bed loading versus temperature response observed for the fully exchanged material.
3. NO and NO<sub>2</sub> produced small and varied positive and negative effects in loading capacity.
4. The observed effects of water vapor on the loading was also inconsistent and inconclusive.
5. The addition of 1 vol % hydrogen to the inlet stream resulted in increased bed loadings at the lower silver contents.

This probably is the result of maintaining more of the limited amount of silver in the reduced state.

Silver utilization averaged 72% for both 1.5 and 3.0% LAg°Z, whereas silver utilizations of over 50% were rare with the fully exchanged Ag°Z. The highest silver utilization reported at ORNL for AgZ was 64%.

#### 5.2.5 Alumina Silicates

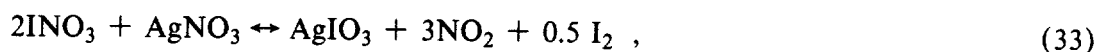
Another class of inorganic sorbents for iodine and methyl iodide removal is silicic acid and aluminum oxide to which silver nitrate has been added. The West German iodine removal effort has been developed around a once-through process using AgNO<sub>3</sub> impregnated amorphous silicic acid (under the trade name AC-6120), which is commercially



available in Europe. Work has also been subcontracted to the University of Belgrade, Yugoslavia, by the EPA to examine the potential for iodine removal for various nitrates on Alcoa alumina H-151.

#### 5.2.5.1 Chemical mechanism

The silver nitrate in the alumina silicate structure reacts with elemental iodine by the following reactions (Wilhelm, 1977):



where the silver and iodine form either silver iodide or silver iodate. Alkyl halides also react with the silver to form silver iodide.



The end products of both reactions with silver are stable solids with low solubilities in water.

#### 5.2.5.2 H-151

A limited amount of information is available on the Yugoslavian work with H-151 (Gal et al., 1974). The chemical composition of H-151 is given in Table 8. Tests have been performed with impregnations of the following metal nitrates: Ag, Cu, Pb, Cd, Zn, Ni, Co, Ce, Ag + Cu, Ag + Ce, Ag + Cd. Of these metal nitrates, only silver and, to a lesser degree, copper and lead, showed irreversible chemisorption of methyl iodide at 56°C. The capacity of cadmium nitrate to bind  $\text{CH}_3\text{I}$  increased at 96°C to nearly that of silver nitrate in dry air.

Thermodynamic calculations indicated that silver oxide, AgO, might be a better choice than silver nitrate and that silver nitrate is better than the other metal oxides tested. Later studies revealed that AgO was superior only in a dry environment.

Tests also showed that the presence of water vapor decreased with  $\text{CH}_3\text{I}$  adsorption efficiency, which has been seen in other systems. An increase in gas velocity also decreased removal efficiency.

The best results obtained for  $\text{AgNO}_3$ -impregnated alumina (7.4 wt % Ag) with a particle size of 0.08 to 0.16 cm were 99.9% retention with a face velocity of 8 cm/s and a relative humidity of 27% at 50°C. The  $\text{CH}_3\text{I}$  loading was 1.9 mg per gram of adsorbent.

Table 8. Specification of base alumina<sup>a</sup>

Composition, %	
Al <sub>2</sub> O <sub>3</sub>	90.0
Na <sub>2</sub> O	1.4
Fe <sub>2</sub> O <sub>3</sub>	0.1
SiO <sub>2</sub>	1.7
Loss on ignition (1100°C)	6.0
Surface area, m <sup>2</sup> /g	390
Bulk density, packed, lb/ft <sup>3</sup>	53
Specific gravity	3.2
Particle sizes, cm	0.34 and 0.12

Source: Gal et al., 1974.

<sup>a</sup>Base adsorbent: Alcoa alumina H-151

### 5.2.5.3 AC-6120

In 1970, Wilhelm and Schuttelkopf (1970) introduced the use of several catalyst carriers impregnated with AgNO<sub>3</sub> for removal of iodine from gas streams at elevated temperatures and from gas streams containing acid vapor. These carriers (KTB, KTC, KTD) were experimental products from the West German chemical company, Bayer, and had a porosity greater than 50% and a specific surface of about 110 m<sup>2</sup>/g.

Early experiments using a bed depth of 10 cm showed high removal efficiency (>99.9944%) for CH<sub>3</sub>I on 1.6-mm pellets with an impregnation of ≤7.8 g Ag/100 g sorbent. Methyl iodide loadings of 1 to 2 mg of CH<sub>3</sub>I per gram of sorbent were obtained at 30°C, and a relative humidity of 70%. However, at 100% relative humidity, the removal efficiency dropped to 27%. Tests using superheated steam showed removal efficiencies greater than 99.9984%. High iodine removal efficiencies (>99.44) from a gas stream containing 8 to 10% NO<sub>2</sub> were also obtained for KTC impregnated with 7.8 to 10.4 AgNO<sub>3</sub> per 100 g. The removal efficiency varied directly with the bed depth and inversely with relative humidity and loading. It was also noted by the workers that an iodine compound less readily adsorbed than CH<sub>3</sub>I was present and that KTC material had a very low efficiency for its removal. Initial economic studies indicated that because of the low silver content of KT materials (18 or fewer grams of silver per Ag 100 g sorbent), the cost would be about three times more than impregnated carbon and nearly three times less than silver zeolite.

In later studies by Wilhelm and Schuttelkopf (1972), Ag-KTB was shown to have higher mechanical strength and abrasion resistance than the other KT products. Ag-KTB has since become available under the product number AC-6120. Both Ag-KTB and Ag-KTC have similar removal efficiencies with equal AgNO<sub>3</sub> impregnation. The normal impregnation was 60 to 80 mg of silver per gram of KT material. Because of the detrimental effect of water vapor on removal efficiency, it was recommended that 70% relative

humidity should be the practical limit in operation. It was also shown that 150°C was the optimum operating temperature. There is, however, a slight increase in removal efficiency above 200°C, but tests were run with NO<sub>2</sub>. The results indicated a small decrease in efficiency from 99.99961% to 99.9973% for 1% NO<sub>2</sub> to 10% NO<sub>2</sub>, respectively. Loadings in excess of 10 mg of CH<sub>3</sub>I per gram AC-6120 resulted in drastic decreases in removal efficiency. The removal efficiency of AC-6120 did not seem to be influenced by irradiation up to  $8.6 \times 10^8$  rad.

In a paper presented at the 1976 ERDA Air Cleaning Conference, Wilhelm, Furrer, and Schultes (1976) discussed the application of AC-6120 for iodine removal in a fuel reprocessing plant. Also included were test results from the high-impregnation version AC-6120/H1 with 12 wt % silver as compared to AC-6120 with 7 wt % silver. If 100% of the silver reacts, 143 g of <sup>129</sup>I could be removed by 1 kg of AC-6120/H1; 75 to 94% utilization is normal. DFs of 10<sup>4</sup> were usually achieved for loadings of about 60% utilization.

Tests were run to examine the effects of various organic iodides. Primary, secondary, and tertiary alkyl iodides all reacted, but the rate of reaction decreased with chain length, and tertiary alkyl iodides reacted much faster than primary or secondary alkyl iodides. Iodocyclohexane and benzyl iodide both reacted at temperatures up to 180°C with the AgNO<sub>3</sub> in AC-6120. The principal reaction has been shown (Hebel and Cottone, 1982) to be:



when *R* = alkyl, cyclohexyl, or benzyl. It has also been shown that alkanes are formed from primary alkyl iodides and that unsaturated hydrocarbons are formed from secondary and tertiary alkyl iodides. Phenyl iodide failed to react up to 180°C. In the presence of water, potentially explosive alkyl nitrates are converted to alcohols.

Studies using dodecane and tributyl phosphate (TBP), which are expected in the vessel off-gas indicated that dodecane was completely inert with respect to AC-6120 and that TBP was converted to a silver phosphate of undetermined structure. AC-6120 also showed signs of extreme discoloration accompanied by a substantial decrease in efficiency; the decrease was attributed to the conversion of the AgNO<sub>3</sub> to Ag<sub>2</sub>O. A NO<sub>2</sub>-air mixture eliminated the discoloration and largely restored the efficiency. A low NO<sub>2</sub> content in the off-gas was also found to control the poisoning of AC-6120 filters. The silver in AgNO<sub>3</sub> was reduced to metallic silver by NO, and the removal efficiency was also reduced by NO. This effect was also reduced by the presence of NO<sub>2</sub>, which reoxidizes the silver.

Since 1977, AC-6120 adsorbent beds have been used to recover <sup>129</sup>I with DFs of 100 at loadings up to 80% bed capacity (Furrer et al., 1978). During one 20-month operating period, two filters containing AC-6120/H1 were used in series achieving up to 98% use of the bed capacity in the first bed (Wilhelm, 1983). The operating parameters were presented by Wilhelm and Furrer (1976) as:

Bed capacity	26 kg of AC-6120
Gas rate	148 m <sup>3</sup> /h
Residence time	1.0 ± 0.4 s
Temperature	130°C
NO <sub>x</sub>	<2 vol %
Service life	120 d at 60% loading

Extensive testing of AC6120/H1 has been conducted in the French "SIROCCO" test rig (Bruzzzone et al., 1983) in preparation for use in the UP3 facility. Tests have been conducted using both I<sub>2</sub> and CH<sub>3</sub>I. High DFs (>10<sup>3</sup>) were achieved for CH<sub>3</sub>I loadings below 80 mg/g and for I<sub>2</sub> loadings below 140 mg/g. The nominal operating temperature was 150°C with a face velocity of 11.2 to 20.1 cm/s for the annular filter cartridge design.

#### 5.2.5.4 Process capacity

For AC-6120/H1, the maximum theoretical loading is 143 mg of I<sub>2</sub> per gram of AC-6120/H1; for AC-6120, the maximum loading is 73 mg of I<sub>2</sub> per gram of AC-6120. With a single AC-6120 cartridge under the West Germany reprocessing plant (WAK) conditions, 60% utilization of the silver can be obtained with an iodine DF above 10<sup>4</sup>. With a two-cartridge system, silver utilizations above 95% can be achieved. At this iodine loading, 46 Ci of <sup>129</sup>I and associated <sup>127</sup>I and <sup>81</sup>Br fission products (340 kg total) would produce 2,700 kg of AC-6120/H1 waste of about 3 m<sup>3</sup> in volume. Actual organic iodide loading of AC-6120/H1 and AC-6120 should be limited to 10 mg CH<sub>3</sub>I/g sorbent. The 7.4% AgNO<sub>3</sub>-impregnated H-151 has a theoretical capacity of 88.2 mg of I<sub>2</sub> per gram of sorbent. H-151 required an even lower load limit of 2 mg of CH<sub>3</sub>I to achieve removal efficiency above 99.9%.

#### 5.2.5.5 Advantages and disadvantages

Alumina silicates offer many of the same operating advantages of silver zeolites and some unique to the material. These are summarized as follows:

1. Iodine is chemisorbed to the silver in a solid suitable for long-term disposal.
2. AC-6120 and AC-6120/H1 can achieve high silver utilization, thus making the sorbent cost attractive.
3. AC-6120 and AC-6120/H1 are not adversely affected by NO<sub>2</sub>.
4. The NO<sub>2</sub> from the dissolver will serve to partially protect the AC-6120 or AC-6120/H1 filter from poisoning.
5. High removal efficiency of AC-6120 and AC-6120/H1 results when in a superheated steam environment.

6. H-151 offers a good removal efficiency at low temperatures.
7. AC-6120 and AC-6120/H1 offer high removal efficiencies between 100 and 200°C; 150°C is the optimum temperature for the AC-6120 and AC-6120/H1 filter.
8. Radiation does not adversely affect the efficiency of AC-6120.

The disadvantages are:

1. H-151 is adversely affected by relative humidity at low temperatures.
2. AC-6120 and AC-6120/H1 are adversely affected by some organics.
3. AC-6120 shows poor removal efficiency above 70% relative humidity.
4. AC-6120 should not be used above 250°C for extended periods of time (Holladay, 1979).

### **5.2.6 Resins**

The possibility of using resins to remove iodine has been examined by several researchers. Much of this work involved iodine removal from liquid streams, however, some limited studies were carried out in gas streams. For the most part, this work was performed to find iodine sorbents less expensive than silver impregnated ones or more stable than carbon.

Ion-exchanged resins are known for their adsorption and exchange properties. They have also been found to have good chemical stability. The macroreticular structure of the resins permit solutions to diffuse completely through the resin.

#### **5.2.6.1 Chemical mechanism**

Little work has been done to determine the mechanism by which elemental iodine or organic iodine reacts with the resins. In general, macroreticular resins exhibit attraction for substances because of their hydrophobicity or hydrophilicity. Because these resins are mainly nonionic in function, they show strong attraction for uncharged molecules, such as elemental iodine or organic iodine, and they show only weak attractions for ionic iodide compounds.

### 5.2.6.2 Varion KS

Hirling (1968) reported on the efficiencies of various filter packings. Among the materials studied were Varion KS (a cation-exchange resin), silica gel, and polypropylene fibers. Tests showed that removal efficiencies were quite low (<40%) at high loadings (875 mg of  $I_2$  per gram of sorbent). At these loadings the beds may have been saturated, therefore, the results do not reflect the actual filter efficiencies. After silver impregnation, Varion KS removed HI with an efficiency of 93.1% at a loading of 1,437 mg of HI per gram of sorbent.

### 5.2.6.3 Amberlite resin

Moore and Howerton (1970a) studied the applicability of the Amerlite series of sorbents from Rohm & Haas Company for iodine removal. The initial studies (Moore and Howerton, 1970a) indicated that Amberlite resins XAD-2 through XAD-12 were capable of producing DF's greater than  $10^4$  for loadings of up to 213 mg of  $I_2$  per gram of sorbent. These studies were conducted in dry air at 21°C with an airborne iodine concentration of  $3 \times 10^3$  mg of  $I_2$  per cubic meter. Later studies (Moore and Howerton, 1970b) with XAD-12 showed that there was some decrease in efficiency as the bed temperature was increased. Some of the iodine sorption capacity from XAD-12 was also lost in the presence of moisture. DFs of  $10^3$  to  $10^4$  were obtained for  $CH_3I$  removal using XAD-12 in dry air; loadings for  $CH_3I$  were low (10 to 84 mg of  $CH_3I$  per gram of sorbent). Increasing temperature adversely affected  $CH_3I$  removal. Additional studies on polystyrene, polyurethane foam, and polypropylene were discontinued due to their very low capacity for elemental iodine.

XAD-12 was also compared to silver zeolite, iodized carbon, and Dowex 1-X4 (an anion exchange resin) (Moore and Howerton, 1971a) (Ferguson et al., 1971). The Dowex 1-X4 and AgX both showed lower capacities than the iodized carbon or XAD-12.

Moore and Howerton (1971b) examined the effects of humidity on the capacity of XAD-4 and XAD-12. DFs greater than  $10^3$  were obtained at 60% relative humidity at 25°C with loadings of 50 mg of  $I_2$  per cubic centimeter of sorbent.

The effects of radiation exposure have been studied by several workers. Bhagwandas et al. (1976) and Hingorani and Venkateswarlv (1976) looked at the effects on both Ag-impregnated and unimpregnated Amberlite IR-120. Negligible radiation effects were noted on unimpregnated IR-120 up to  $1 \times 10^7$  rads; however, as the dose rate was increased to 17 mrad, the capacity decreased to 61% of the original amount. The removal capacity of the silver impregnated sorbent showed no effect up to  $2 \times 10^8$  rads. This contrast may be a result of surface oxidation of the IR-120 and the silver-impregnation protection of the surface from such oxidation reactions. Huh, Donalson, and Johnson (1974) examined the radiation-induced bonding of iodine to polystyrene. This work was done in aqueous suspensions with a population composed of  $1.4 \times 10^{-12}$  particles ( $0.234 \mu m$  in diameter) per cubic centimeter. Bonded to the surface are 0.02 iodine atoms per 100 eV of energy; this iodine was not removed by washing or exposure to anion exchange.

#### 5.2.6.4 Process capacity

The maximum loading of elemental iodine on XAD-12 was 1.39 g of  $I_2$  per gram of sorbent at 25°C from dry air; 84 mg of  $CH_3I$  per gram of sorbent was the maximum loading of organic iodide on XAD-12 at 50°C from dry air. For XAD-4, the maximum loadings were 278 mg of  $I_2$  per gram and 15 mg of  $CH_3I$  per gram of sorbent from dry air at 21 to 25°C. The airborne iodine concentration was 1 to  $4 \times 10^3$  mg of iodine per cubic meter.

#### 5.2.6.5 Advantages and disadvantages

Resins appear to offer advantages similar to those of other solid sorbents. In addition, resins offer the following:

1. The macroreticular resins are acid resistant and thus may function well in gas streams containing  $NO_x$ .
2. They exhibit high  $I_2$  capacity.
3. They show good resistance to radiation damage.

The limited amount of work with these materials also indicates the following disadvantages.

1. They are adversely affected by humidity and elevated temperature.
2. There are limited experience and information available on iodine removal from gas streams.

## 6. WASTE FIXATION

### 6.1 DISPOSAL CRITERIA

A major obstacle in selecting a storage or disposal form for iodine is that criteria have not been established. Without these criteria, there is no quantitative measure for the relative importance of such factors as thermal stability of the waste form, leach resistance of the package, long-term integrity of the container, and the role of isotopic dilution.

Burger (1980) attempted to establish a set of guidelines for establishing such criteria. This report describes the global quantity, distribution, and rate of movement of  $^{127}\text{I}$ , naturally produced  $^{129}\text{I}$ , and "man-made"  $^{129}\text{I}$ . The  $^{129}\text{I}$  resulting from nuclear activities over the past few decades is not uniformly dispersed; therefore, the possibility of greater dispersion exists. Thus, the potential for large scale planned dilution was considered. The potential for dilution with respect to either the  $^{129}\text{I}$  concentration or the  $^{129}\text{I}$ : $^{127}\text{I}$  ratio far exceeds the minimum required for acceptable exposure. For the utilization of dilution principle, it is preferable to package and dispose of the  $^{129}\text{I}$  separately from the other fission products. With regard to dilution, deep ocean disposal can be seen as a logical approach.

There is no way to predict the ultimate stability and, hence, the lifetime of a specific storage form over extremely long time periods. Therefore, it must be assumed that whatever the final waste form is and wherever it is stored, the material will be exposed to water and/or high temperature at some point in time.

In a wet environment, a concrete iodine-containing matrix will lose iodine by erosion and diffusion once the containment is breached. Studies with barium iodates by Clark (1977) and Morgan et al. (1978) have shown leach rates on the order of  $10^{-4}$  cm/d. It may be possible to lower these to  $10^{-6}$  cm/d. Assuming the lower leach rate was applied to a cylinder of iodine-containing concrete 0.3-m radius by 1 m, an iodine release rate of 0.003%/year would result. This is a significant fraction when considering the  $1.7 \times 10^7$ -year half-life.

Burger (1980) presents a number of factors which must be considered in determining the criteria for  $^{129}\text{I}$  disposal. These are the following:

#### Technological

1. Acceptability of secondary wastes from process
2. Acceptability to all parts of fuel cycle
3. Presence or absence of other radioactivity



4. Compatibility with environmental conditions encountered during processing, storage and transportation (including accidents)
  - a. Packaging
  - b. Thermal characteristics
  - c. Solubility
  - d. Interaction with other chemical species
5. Reliability, safety, and simplicity

#### **Economic**

1. Monetary cost
2. Material resources and energy expended
3. Manpower commitment

#### **Environmental**

1. Capacity of the environment and distribution of  $I^{129}$
2. Health impact resulting from control
3. Presence or absence of other hazardous materials

#### **Sociopolitical**

1. Adaptability to a changeable social and political environment
  - i. Stability of institution
  - ii. Public perception
  - iii. Impact of future technology
2. International agreements
3. Radioactive half-life of  $^{129}I$  on same order of magnitude as that of major geologic changes

Based on these factors, it was suggested that preliminary standards be developed to apply to (1) temporary storage and transportation, (2) disposal to a dry environment with a time limitation on calculated behavior, and (3) disposal to the deep ocean with complete release allowed in 1,000 years.

Hebel and Cottone (1982) provide seven criteria for the selection of an immobilization form for  $^{129}I$ . These are:

1. Thermal stability. Generally limited to 65°C and in the worst case to 250°C. Stability in this context is limited to preventing volatilization of iodine in any form whether by sublimation or decomposition.
2. Resistance to water. Low leachability and low solubility.
3. Resistance to oxidation and reduction. The waste form should be stable in air under moist as well as dry conditions. If anaerobic conditions arise, it should be stable toward reductants.
4. Compatibility with its container.
5. Compactness. This is tempered by the relatively small amount of iodine present in the spent fuel.
6. Low cost. This is also not a highly critical element because of the amount of iodine involved. The cost of silver could have some impact, however.
7. Ready preparation. A viable process must exist from the recovery step on.

## 6.2 IODINE FIXATION FORMS

A number of possible immobilization forms have been suggested. These generally fall into four broad categories of options.

1. Inorganic iodides and iodates of low solubility.
2. Solid sorbents (e.g., zeolites loaded with iodine).
3. Cementitious materials containing (1) or (2).
4. Low-melting-point glasses.

Hebel and Cottone (1982) indicate that options 1 and 2 provide the possibility of retrieving the iodine at some later date if it is desirable to change its form, while options 3 and 4 virtually rule this out.

An excellent review of the candidate immobilization forms is also provided by Hebel and Cottone (1982). In the class of inorganic iodine compounds, the choice fell mainly on  $\text{Ba}(\text{IO}_3)_2$ , primarily on the grounds of its relatively low solubility. However, only  $\text{Hg}_2\text{I}_2$ ,  $\text{AgI}$ , and  $\text{Hg}_2(\text{IO}_3)_2$  have solubilities low enough not to exceed the maximum permissible concentration in drinking water.  $\text{Ba}(\text{IO}_3)_2$  requires a dilution factor of 5,500 to maintain the same concentration limits but do not require the handling of mercury. If considerations are extended to include stability toward heat, water, and oxidation/reduction reactions, only  $\text{AgI}$  appears viable as a stand-alone waste form. Many more compounds may be considered if the iodine compound is to be incorporated into a matrix of some type.

A number of iodides and iodates have been evaluated for incorporation into cements at levels up to about 10% iodine by weight. Of these  $\text{AgI}$  and  $\text{Ba}(\text{IO}_3)_2$  appear as top choices.  $\text{Ba}(\text{IO}_3)_2$  is favored on cost grounds and has the advantage of ready preparation

from the product of the Iodox process. Tests have identified a number of parameters that beneficially reduce the leach rate of the iodine from the cement matrix. These are:

- Reducing the temperature.
- Reducing the water-to-cement ratio.
- Reducing the iodine content.
- Avoiding incorporation of soluble iodine.
- Curing the cement in a  $\text{CO}_2$  atmosphere.
- Adding certain substances to the grout mixture such as:
  - 0.5%  $\text{Na}_2\text{SiO}_3$
  - 0.5%  $\text{H}_2\text{SiF}_6$
  - 0.9% butyl stearate
  - 1.2% polybutene
  - 10% fly ash
  - 0.014 mol/kg  $\text{Ag}^+$
  - 0.056 mol/kg  $\text{Ba}^{++}$ .

The spent, iodine-loaded, silver-containing sorbents may themselves constitute a suitable immobilization form which only requires packaging. This has been proposed for AC 6120 (Wilhelm and Furrer, 1977) and may also apply to the zeolite waste forms (Burger, Scheele, and Weimers, 1981).

One consequence of using silver-containing material as a waste form is that the silver is not recovered. However, as pointed out earlier, these costs are relatively small.

Only limited information is available regarding the suitability of the iodine-loaded sorbents as immobilization forms. Some of the available information comes from attempts to identify the chemical forms of the iodine present on the sorbent. Thermal stability is assumed up to the operating temperature of the sorbent material. Burger and Scheele (1981) indicated that much of the iodine could be removed from AgZ as the temperature of the material approached  $500^\circ\text{C}$ . Their work also indicated that greater than 50% of the iodine sorbed on AgX could be removed using carbon tetrachloride, tetrachlorethylene, toluene, and similar solvents using a soxhlet technique. However, none was extracted from AgZ using the same methods.

While it is possible to regenerate the loaded AgZ and trap the HI on PbX, the long-term stability of the PbI material is in question. Observations at ORNL (Jubin, 1987) indicate significant iodine volatilization if the loaded PbX material is exposed to oxygen even in a sealed container.

Burger and Scheele (1981) reported that fixation in Portland cement, may be a viable alternative for several compounds (e.g., group II iodates). They also found that iodine-loaded zeolites can also be mixed with cement, producing a product of good physical properties. However, the leach resistance of the monolith was no better than of the zeolite itself.

The stability and chemical inertness of glasses and the relatively low surface areas of chemical attack make them attractive as mediums for immobilizing various radioactive wastes including iodine.

The dissolution of NaI or KI in standard fluoride glasses ( $\text{ZrF}_4\text{-BaF}_2\text{-ThF}_4$  or  $\text{SrF}_4\text{-BaF}_2\text{-LaF}_3$ ) is limited to 1 mol %. These glasses have a melting point of  $600^\circ\text{C}$  compared to  $>1,000^\circ\text{C}$  for classic silicate and borosilicate glasses. The quaternary glasses  $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-BaI}_2$  and  $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-NaI}$  permit compositions of 4 and 8% iodide respectively. Unfortunately, these glasses are quite susceptible to leaching by aqueous solutions. Malagani et al. (1978) have developed a halophosphate glass capable of incorporating 10–20% iodides.

### 6.3 CONVERSION PROCESSES

#### 6.3.1 Caustic Scrub Liquors

Methods to prepare CuI and  $\text{PbI}_2$  have been developed in France (Chensne et al., 1977; Anav et al., 1974). CuI is prepared by acidifying the scrub liquor and adding cupric nitrate in the presence of hydrazine at  $\text{pH}_2$ . The CuI is then precipitated and filtered. The lead iodide is prepared by first liberating the iodine in the elemental state by oxidation. The free iodine is then contacted in a countercurrent scrub tower with a lead nitrate/hydrazine nitrate solution. At the  $60^\circ\text{C}$  process temperature, the lead iodide is soluble, but as the solution cools, it precipitates and can be filtered off. The solubility of both compounds is such that long-term stability is in doubt.

#### 6.3.2 Iodex Process Products

The recommended conversion step converts the soluble iodic acid into insoluble  $\text{Ba}(\text{IO}_3)_2$  by simple reaction with  $\text{Ba}(\text{OH})_2$ . Excess  $\text{Ba}(\text{OH})_2$  should be used to ensure complete reaction and does not affect the cement stability.

#### 6.3.3 Mercurex Process Products

The  $\text{Hg}(\text{IO}_3)_2$  from the Mercurex process is recovered via filtration. The material can then be incorporated into cement. An alternate process involves the contacting of the process solutions with caustic soda to produce  $\text{NaIO}_3$  followed by conversion to  $\text{Ba}(\text{IO}_3)_2$  as described for the Iodex process.



## 7. SYSTEM DESIGN CONSIDERATIONS

Airborne waste management is a complex set of interdependent operations which must be integrated into a complex processing system. A simple combination of individual retention steps does not necessarily lead to the design of a suitable DOG system. The system has to be conceived as a unity and must be compatible with the preceding process steps as well as the subsequent waste treatment processes. The selection of processing steps for the off-gas train stems from an evaluation of:

1. Plant size
2. Fuel age
3. Ventilation philosophy
4. Subsequent processing steps
5. Preceding processing steps
6. Regulations governing emissions
7. Selected disposal modes.

### 7.1 PLANT SIZE

The size of the plant can lead to the selection of certain types of equipment or processes over other types. This is especially true in the selection of iodine removal equipment. In small facilities the cost of liquid-scrubbing methods such as Iodox is prohibitive, whereas in much larger operations the cost of using silver-exchanged sorbents can easily outweigh the capital and operating costs associated with the liquid methods. The design of a liquid system for a larger plant would probably be directed towards removal of the bulk of the iodine from the DOG and would still use silver-containing sorbents for polishing the DOG and for the treatment of the VOG.

A second factor associated with plant size is the in-leakage to the process streams. In general, it is expected that the inleakage to the off-gas systems is not a linear relationship with plant size; therefore, the larger the facility, the higher the concentrations of the airborne radionuclides in the off-gas streams.

### 7.2 FUEL AGE

The fuel-age question is virtually self-evident. The age of the fuel goes hand-in-hand with the regulations governing the emissions from the plant site. In terms of iodine, if the fuel has cooled more than 200 d, the only iodine isotopes of any consequence are  $^{129}\text{I}$  and

<sup>127</sup>I. Obviously when dealing with short-cooled fuels, <sup>131</sup>I becomes a factor in the calculations of the required plant iodine DF. In addition, the decay heat from the short-half-life material must be considered.

### 7.3 VENTILATION PHILOSOPHY

Two primary objectives provide basic direction to the design of off-gas treatment processes. First, the airborne radionuclides should be contained to a small plant volume. This prevents dispersion throughout the facility and obviates additional and expensive control measures on large plant volumes. Second, the airborne radionuclides should be concentrated in a single, small waste stream. This avoids large, extensive secondary waste stream treatment steps.

To date, the off-gas streams from nuclear facilities have been quite large, resulting in very dilute radionuclide concentrations. The large volumes of gas which require treatment limit the viable process selection simply to size and cost considerations. The stream size also limits the extent to which the effluents can be treated. Efforts in both the United States (Spencer, 1987) and the Federal Republic of Germany (Henrich and von Ammon, no date) have been directed at reducing the size of the VOG stream by orders of magnitude.

The main portion of the ventilation off-gas arises from the processing cells and is only slightly contaminated under normal operation. The reduction of the large off-gas volumes associated with the VOG can be advantageous because of cost and safety factors. In addition, the small off-gas volumes can be purified more readily and in smaller equipment.

The large-cell off-gas volumes, which are generally treated along with the actual VOG, result from the high exchange rate of air through the cell. The high rate is used primarily to provide cooling and not to control contamination in the cell atmosphere. As an alternative, temperature control can be achieved by the use of in-cell coolers. In the U.S. design for low-flow ventilation, the temperature is controlled via the addition of N<sub>2</sub> to the cell, which, in turn, affects the pressure. The pressure itself is quickly adjusted by the coolers. Figure 4 shows this control scheme. A second benefit of this control method is the rapid detection of nitric acid leaks into the cell through the presence of acid in the condensate from the in-cell coolers. This type of cell off-gas system can reduce the total VOG/cell off-gas by at least two orders of magnitude.

Should low-flow ventilation be selected, it impacts the design of the head-end equipment as well and the general concept of air handling in the rest of the facility. The head-end should strive to contain the bulk of the volatile and semivolatile fission products in as small a volume of gas as possible. Extensive efforts should also be made to minimize any release of radionuclides to the cell so as to reduce the requirements for treatment via the VOG system. The rest of the plant should be designed to minimize the usage of air. This reflects onto the design of air-lifts, air motors, and various air-purge systems that might be employed in the facility.

The dilution to the DOG resulting from in-leakage through the shear, dissolver, and deliberate gas additions can itself result in various options in the design of the DOG system. For very small plants in terms of heavy metal throughput, the NO<sub>x</sub> concentration

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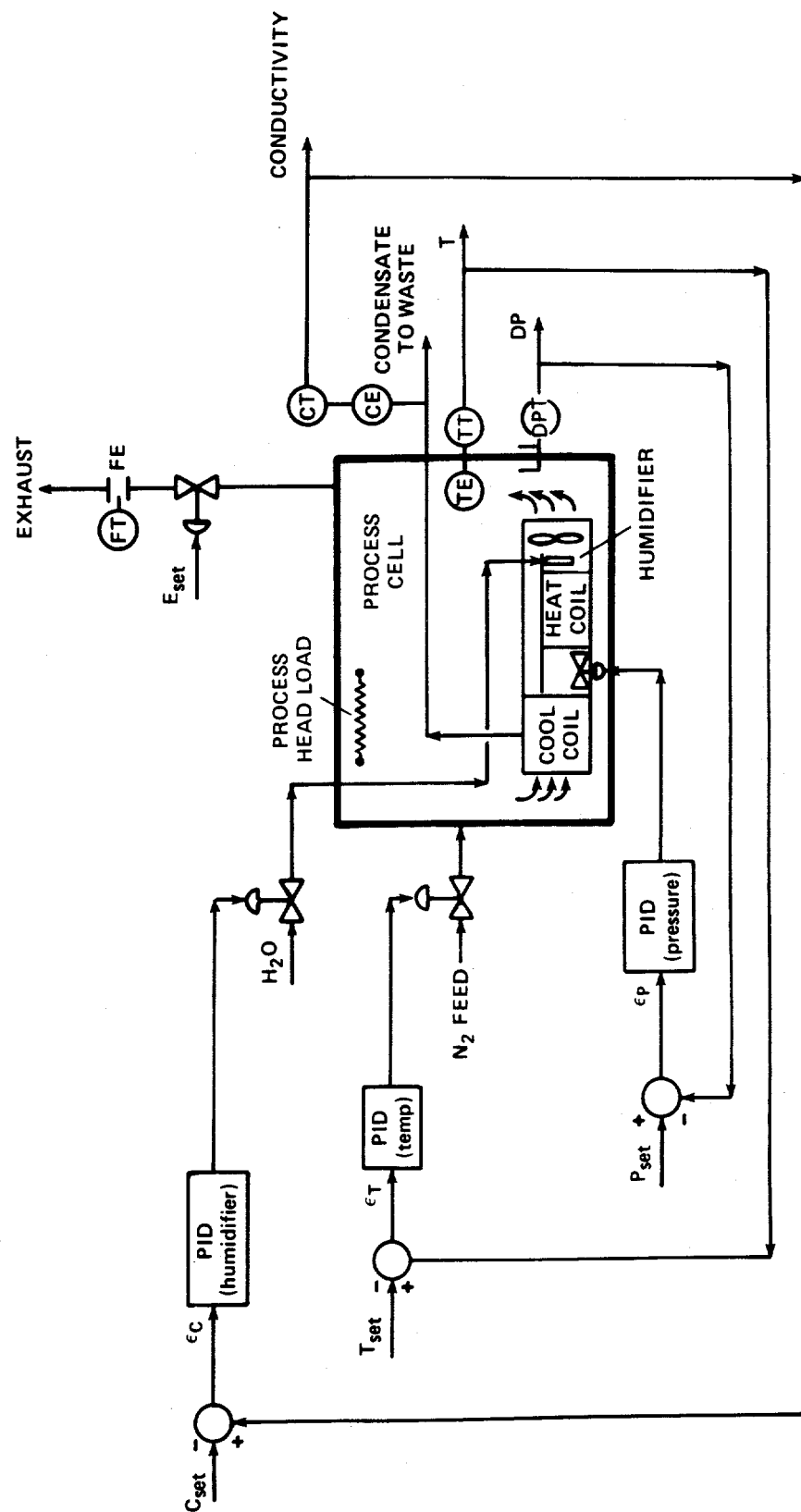


Fig. 4. Control strategy for a low-flow ventilation system.



may be so low that conventional aqueous scrubbing may be ineffective or completely unnecessary depending on subsequent processing requirements. Henrich and Hufner (1984) presented a number of potential DOG flowsheets describing processing options depending on the dilution of the DOG stream, Figure 5. These options covered off-gas rates from 25 m<sup>3</sup> (STP)/h to 750 m<sup>3</sup>(STP)/h and focused primarily on the extent to which NO<sub>x</sub> and iodine are treated.

## 7.4 SUBSEQUENT PROCESSING STEPS

Once the "iodine free" DOG leaves the final iodine polishing step, subsequent processing is generally limited to Kr and CO<sub>2</sub> removal (if required) followed by a final HEPA filtration step prior to discharge to the stack. If <sup>85</sup>Kr retention is justified, then the subsequent handling of the recovered rare gases to provide either a stable form for long-term storage or to utilize the recovered gases must be addressed.

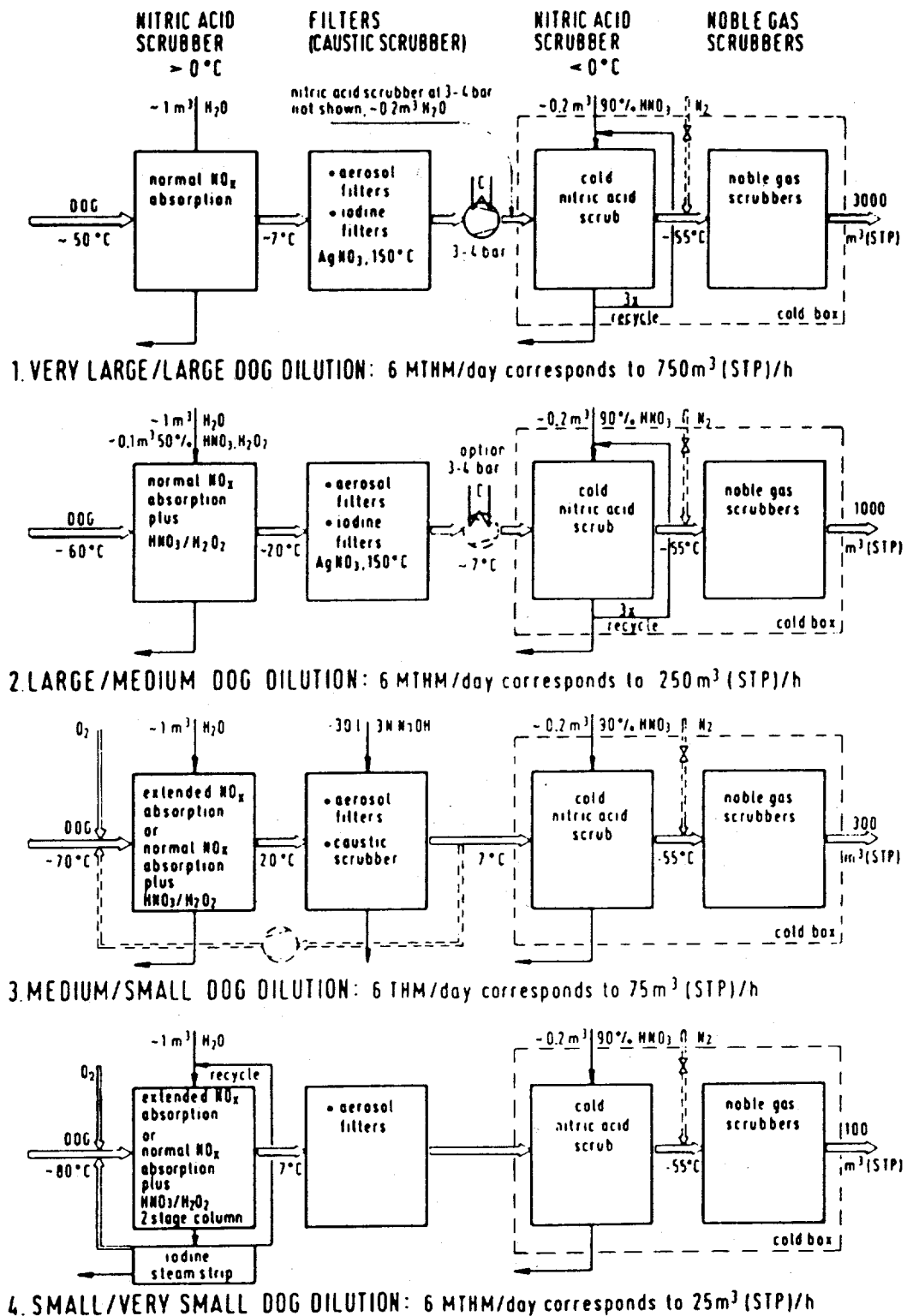
There are two primary methods available to recover <sup>85</sup>Kr. These are the selective adsorption process (Eby et al., 1982; Henrich and Ebert, 1985) and the cryogenic krypton recovery process (von Ammon et al., 1983; Hebel and Cottone, 1983).

### 7.4.1 Cryogenic Distillation

Cryogenic distillation is a technology to recover rare gases that has been used commercially for many years. When applied to dissolver off-gas, the gases must be pretreated to remove interfering constituents, thus ensuring system safety and operability. All gases that would condense at liquid nitrogen temperatures would have to be removed to prevent plugging of the equipment. These include NO<sub>x</sub>, water vapor, and CO<sub>2</sub>. Oxygen must also be removed to avoid the formation and accumulation of ozone. Separations in the process occur because of differences in the boiling points of the gases. Krypton and xenon are then removed from the off-gas stream in a stripping column by dissolution in liquid nitrogen or oxygen. These are then subsequently separated in the purification columns, where first the solvent is removed along with most of the impurities and then the krypton is boiled off from the xenon.

### 7.4.2 Fluorocarbon Absorption

The basis for this recovery process is the solubility difference that exists between the various gas compounds in the solvent chosen for the process. The process consists of absorbing the noble gases and several other constituents from the off-gas stream and then stripping the gases out of the solvent. The solvent selected for the process was CCl<sub>2</sub>F<sub>2</sub> or R-12. R-12 was selected because of its noble gas absorption capacity, noble gas/bulk gas separation factors, and relatively good thermal and radiation stability. In 1967, the development of the process was initiated at the Oak Ridge Gaseous Diffusion Plant (ORGDP) as a conceptual study for core meltdowns related to a reactor safety study. Since then, the development has addressed applications to routine reactor operations and



Source: E. Henrich R. Hufner, "Modular Design of a Reprocessing Plant Dissolver Off-Gas System," International Conference on Radioactive Waste Management, International Atomic Energy Agency, Seattle, WA., May 1983.

Fig. 5. DOG purification systems. Source: Henrich, 1984.

off-gas treatment for reprocessing plants. The ORGDP development has progressed through three generations of pilot plants (Little et al., 1983). The technology development has been described in a series of reports (Stephenson and Eby, 1976; Merriman et al., 1980; Little et al., 1983; Eby et al., 1982).

Early work in the U.S. focused on the use of three separate columns to perform the absorption, intermediate stripping or fractionation, and final stripping operations. However, since 1978, the process development has been conducted in a single column, which serves all three functions.

The krypton product from the selective absorption process is obtained through a product purification process in which other contaminant gases are removed. The product stream, as it leaves the single column, is expected to be 5% krypton, 33% R-12, 10% light gases, 44% xenon, and 8% carbon dioxide. In the noble gas product purification subsystem, the product stream will pass through a 13-X molecular sieve to remove R-12. The stream then flows through a 5A molecular sieve to remove CO<sub>2</sub>. Silver-exchanged mordenite is used to remove xenon. The final step is to remove the krypton from the light gases by use of a cold trap.

The R-12 trap is regenerated and the R-12 returned to the system. The collected CO<sub>2</sub> is removed by flushing the bed with air. The CO<sub>2</sub> can then either be vented if applicable regulations allow, or trapped for long term storage on Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O (Haag et al., 1986). Xenon can be vented following regeneration of the AgZ beds. The krypton is sent on to an ion implantation process, where it is incorporated into a sputtered metal matrix at pressures on the order of 0.4 Pa (McClanahan, Moss, and Greenwell, 1986; Whitmell, Nelson, and Smith, 1980). The sputtered metal matrix will contain 5–6% Kr on an atomic level.

An alternative process for <sup>85</sup>Kr storage is encapsulation in a zeolite matrix. Work on this method has been conducted in both the United States and the Federal Republic of Germany (Christensen et al., 1981; Penzhorn et al., 1980). Krypton loadings of 50 m<sup>3</sup> of STP per cubic meter solid are readily achieved at 100 MPa in zeolite 5A at 700°C. The krypton is encapsulated by a sintering process where the pores of the zeolite are sealed. Krypton leakage rates are predicted from experimental data to be less than 0.03 and 0.3% for 10-year storage at 300 and 400°C, respectively. The process developed in the Federal Republic of Germany obtains similar results at lower temperatures and pressures.

A third alternative is storage of the recovered krypton in gas cylinders. This method provides for easy recovery of the krypton for subsequent industrial use, but it also increases the hazard of a major release of <sup>85</sup>Kr of potentially greater health risk than the total continuous release of the <sup>85</sup>Kr from the reprocessing plant itself would have been.

## 7.5 PRECEDING PROCESSING STEPS

The primary concerns for processing steps prior to the iodine removal step are to minimize the total volume of the DOG by controlling the in-leakage and to minimize the fluctuations in the DOG flow to the extent possible. A major source of fluctuations can arise through the choice of dissolver technology. In general, a batch dissolver results in a more cyclic DOG flow and composition than does continuous dissolution.

A second item to consider in the iodine removal system is the  $\text{NO}_x$  composition in the off-gas stream to the selected process and the impact of the  $\text{NO}_x$  concentration on iodine removal efficiency.

## **7.6 REGULATIONS GOVERNING EMISSIONS**

As stated before, these provide the basic guidance for determining the required DFs for each isotope. As criteria and regulations for waste forms are developed, these will further focus the selected recovery processes toward the production of viable waste forms.

## **7.7 SELECTED DISPOSAL MODES**

Various waste forms were discussed in the preceding section. The selection of recovery processes is, to a certain degree, governed by the criteria placed on the final waste form and the state to which the waste form itself is developed. As pointed out previously, there are no criteria for nor regulations governing the final waste forms currently in force. To this end, only engineering judgment can be applied as to which forms appear to be the most desirable.



## 8. CONCLUSIONS

Iodine-129 is a radioactive isotope produced primarily in the production of power in nuclear reactors. Its long half-life of 17 million years results in relatively low radiotoxicity when compared to other radioactive wastes, but this same factor makes its confinement from the biosphere virtually impossible to guarantee over time periods on the same order as major geological eras. Sooner or later it might appear in the environment, and thus, it is of global concern.

The selection of off-gas treatment steps cannot be taken as individual processes that can be linked together in just any fashion. The selection of the processes stems from a number of factors and can have significant impact on the design of a new facility. In fact, the design of the off-gas system should not be in any way considered an "add on" to the design, but it must be an integral part of the facility design. Without adequate off-gas systems to control emissions, the licensing of a new facility will most likely not occur.



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